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## WILLIAMSON'S RESEARCHES ON THE CARBONIFEROUS FLORA.

BY the death of Dr. William Crawford Williamson, on 23rd June of this year, English Science lost a fine naturalist of the good old school, who had escaped the narrow specialisation of the present period, and who has left his mark on every department of Natural History. The object of the present article, however, is not to give an obituary notice of Williamson, or to attempt any account of his scientific work as a whole; that has been undertaken elsewhere (by Solms-Laubach, Carruthers, Seward, Lester Ward and others). What is here aimed at is to give a brief statement of the chief results of his researches in the special department of Fossil Botany (the Carboniferous Flora) on which his scientific energies were mainly concentrated during the last twenty-five years of his life.

Williamson's work on fossil plants dates back to the very beginning of his career, for when scarcely twenty he made important contributions to Lindley and Hutton's *Fossil Flora of Great Britain* (36), 1833-37; at least thirty-two of the plates in this classical work were drawn by him, and in most of these cases the letter-press is wholly or in part from his hand. In a paper on the fossil remains of the Yorkshire coast (20), 1836, many vegetable remains are enumerated.

His first important original work on a palæobotanical subject belongs, however, to the year 1851, when he pub-

lished his memoir "On the Structure and Affinities of the Plants hitherto known as *Sternbergiæ*" (21). These curious fossils, in their typical form, are cylindrical bodies, marked with constrictions at very short intervals, so that the whole has been compared to a pile of coins. Williamson was the first to prove that these *Sternbergiæ*, or *Artisiæ* as they were also named, represent casts of the medullary cavity of a *Dadoxylon*, the constrictions marking the position of the diaphragms by which the fistular pith had been chambered. The paper is an admirable one, and the anatomical details of the tissues of the stem were worked out with great accuracy for that period. We now know that *Dadoxylon* was the stem of *Cordaites*, so we see that Williamson, in this early paper, made one of the first contributions towards building up the very complete knowledge which we now possess of this remarkable extinct family of Gymnosperms.

The characteristic work of Williamson, on which his reputation as a leader in Fossil Botany will rest, was that on the microscopic structure of Carboniferous plants. The paramount importance of such studies is, perhaps, hardly appreciated by systematic botanists, who, in dealing with recent plants, are accustomed to rely almost entirely on the more external morphology, and particularly on that of the reproductive organs. Evidence of this kind, however, is often wanting in the case of fossil plants, and when we are dealing with families so far back in the past, and so remote from any now living, as those of the Carboniferous Flora, it is obvious that the mere external characters of *vegetative* organs must be a very insufficient guide. Indeed even where the reproductive organs are preserved, little can be made of them, at any rate if they are Cryptogamic, without reference to their minute structure. Consequently it is hardly too much to say that, as regards the earlier formations, no knowledge of the Flora, which is of botanical value, can be acquired without the aid of histological characters, in addition to those of a more obvious kind.

So far as the Carboniferous strata are concerned there is happily no lack of magnificently preserved material for structural investigation, and it was by the thorough study

of such specimens from British sources that Williamson rendered his great services to Fossil Botany.

It is of interest to learn how these investigations began, and fortunately we are able to explain this in Williamson's own words from autobiographical notes which he left :—

“Early in the fifties when I was commencing in an unsystematic way to grind down fragments of various objects for microscopic investigation, I found in a drawer of my cabinet a portion of a Calamite that had been extracted from one of the ironstone nodules of the Coal-Measures. I was not at that time provided with a lathe or any other form of cutting or grinding machinery for preparing microscopic sections, yet the Calamite presented indications that some structure might be found in it. Chipping off with hammer and chisel such fragments as appeared suitable, I ground them down on a flagstone, and thus succeeded in obtaining nine curious sections showing the structure of a woody zone where it was in immediate contact with the medulla. Having then no intention of making any special use of these preparations, they were put away in a drawer of the cabinet and almost forgotten.”

Our author then goes on to tell how he soon provided himself with some simple machinery for section-cutting, and narrates the lucky chance by which he became possessed of a wonderful cast of the interior of a Calamitean stem, which, in conjunction with the specimens showing structure, did much to elucidate the anatomy (see Williamson, 9, pl. 21, fig. 31; and 22). The publication of a figure of this cast in Lyell's *Manual of Geology*, 1855, led to a correspondence with the French palæontologist, Grand'Eury. This again called Williamson's attention to his old Calamitean slides, which ultimately formed the basis of his paper of 1869, “On the Woody Zone of an Undescribed Form of Calamite” (22). This paper marks the beginning of his more mature work, and is in itself of great interest, for the form described is that remarkable one which he named *Calamopitys*, the nearest approach to a true *Calamodendron* which has been derived from the English Coal-Measures. All other

Calamitean stems so far discovered in this country, belong to the Arthropitoid type, in which the structure of the wood is less complex.

A passage from the autobiographical notes already mentioned refers to this time, and gives an interesting idea of the spirit in which the work was undertaken :—

“ I then formed a resolution which has been of the greatest service to me. Remembering how I had been misled in my early researches amongst the Foraminifera, by the authority of Ehrenberg, I determined not to look up the writings of any other observers until I had studied every specimen in my cabinets, and arrived at my own conclusions as to what they taught. Having thus formed my own independent judgment, I then turned to the works of other observers in the same fields to learn in detail what their views were.”

To this resolution not only the great merits, but also some of the defects of Williamson's work may be traced. All his writings bear the stamp of absolute originality, and are free from the wearisome load of literary recapitulation by which so many modern scientific treatises are burdened. On the other hand, no one man's work can form a sufficient basis for valid generalisation, and in some cases Williamson would doubtless have arrived sooner at true conclusions if he had allowed himself to be a little more influenced by the researches of others.

But no investigator, however independent his spirit, could succeed in making his mind an absolute *tabula rasa* to start with, and so we naturally find some traces of the influence of the great Brongniart in Williamson's earlier papers. In the memoir of 1869 (p. 173) he says: “ The Calamites seem to me to constitute a well-defined link connecting the Exogens with the Acrogens”. Brongniart, as is well known, had in his earlier works united all the Calamites in one group, but had afterwards separated those with exogenous (or, as we should now call it, secondary) growth under the name of *Calamodendron*, reserving the genus *Calamites* for forms supposed to be destitute of secondary tissues. The former he regarded as “Gymnospermous



Dicotyledons" on account of their anatomical similarity to that class, while the latter were left among Cryptogams.

Williamson, in the passage above cited, shows that though already beginning to disbelieve in Brongniart's two groups, he still attached great systematic importance to the presence of secondary tissues.

In the next year our author published a paper "On a New Form of Calamitean Strobilus" (23). This relates to an interesting cone, more fully described at a much later date (14), of the type subsequently placed by Weiss in his genus *Palæostachya* (37) (vol. ii., p. 161), in which the peltate scales arise in or near the axils of the bracts, instead of being inserted midway between their whorls as in *Calamostachys*. Williamson now (1870) arrived at the conclusion that "the Calamites constitute essentially *one* large group of plants". "Their stems were exogenous so far as the woody cylinder was concerned, and closely related to those of the *Dadoxylons*. But on the other hand their fructification was Cryptogamic." He inferred that the Calamites were "a generalised type, afterwards differentiated through the *Dadoxylons* and the oölitic *Equiseta*, into the modern types of Coniferæ and Equisetiform plants". The mere occurrence of secondary growth was no doubt an insufficient basis for such a conclusion, though, in the opinion of the present writer, the possibility of a relationship between Calamariæ and primitive Coniferous Gymnosperms may again have to be considered.

It will be of interest to trace rapidly the further development of Williamson's work on the Calamites. The first memoir of the great series in the *Philosophical Transactions of the Royal Society* is entirely devoted to this group. The author states that "the fundamental aim of this memoir is to demonstrate the unity of type existing among the British Calamites". In other words he showed that all British Calamites, of which the structure can be ascertained, are alike in possessing secondary tissues, and consequently that Brongniart's distinction between Cryptogamic Calamites and Phanerogamic Calamodendra has no existence so far as our native Carboniferous Flora is concerned. In the light of

our present knowledge we can see the great merits of this memoir, though they were hardly appreciated at the time. Conclusive proof is there given of the truth of the view of Germar, Corda, and Dawes, that the ordinary form of preservation of a Calamite is nothing but a cast of the medullary cavity; the significance of the various markings on such casts was rightly explained. The main lines of the anatomy of both old and young stems were accurately laid down, and the existence of true medullary rays in the secondary wood demonstrated, while some evidence as to the mode of branching was already brought forward. This memoir undoubtedly laid a sound foundation for our knowledge of the structure of the Calamitean stem.

Of the later memoirs the most important for the vegetative structure of Calamites is part ix. (1877), which contains a splendid set of illustrations of the anatomy. A series of very young stems are figured and described, and their resemblance at this early stage to stems of recent *Equiseta* is recognised. This had become a point of great importance, for the demonstration that the supposed stems, as shown in ordinary sandstone specimens, were only casts of the hollow pith, had to a great extent cut away the old grounds for regarding the Calamites as Equisetaceous. Consequently accurate anatomical evidence on this point was much needed. The position and mode of attachment of the branches were also very finely elucidated in this memoir, though of course many important details were only made out at a later time. In this paper the genus *Astromylon* was founded, not having been previously distinguished from *Calamites*. A later memoir (part xii., 1882) was largely devoted to *Astromylon*, with which the smaller specimens, described by Hick and Cash (38) under the name of *Myriophylloides*, were identified. It was not till a later time that we learnt the true nature of *Astromylon*, which, as Renault has conclusively proved, is made up of the roots of *Calamites* and its near allies (39). This result has since been amply confirmed by the study of the English specimens. Although Williamson at the time failed to detect this fact, he displayed great acumen in uniting (and, as it has proved, quite correctly) forms so different as

those grouped together under the name *Astromyelon*, in his part xii. We now know that these organs are all roots and rootlets of *Calamites*.

Passing on to Calamarian *fructifications* we find that memoir v. (1873) contains some additional illustrations of the cone now known as *Calamostachys Binneyana*, already described by Binney and Carruthers (41 and 42). These authors had already recognised its true affinities as a form of Calamarian fruit. Williamson was unfortunately misled by a mistake as to the anatomy of the axis, and for many years refused to allow that *Calamostachys* had anything to do with *Calamites*. Ultimately he corrected this error himself, but it affects all his work on the subject up to 1890. The point is this: our author thought that the axis of the strobilus in *Calamostachys* was traversed by a solid strand of wood, something like that of a *Sphenophyllum* or, to use his nomenclature, *Asterophyllites*. In reality there is no resemblance in the anatomy of the two genera, for *Calamostachys* has in fact a well-developed pith, not to mention other differences (15 and 29). This anatomical error logically led Williamson to the conclusion that *Calamostachys* had much closer affinities with *Asterophyllites* (which he then regarded as Lycopodiaceous) than with *Calamites*. In memoir v., however, some interesting additions were made to our knowledge of the fruit, the most important being the first observation of the young spores still enclosed in their mother-cells, the remains of which had been mistaken by a previous observer for elaters.

In 1879 (mem. x.) further valuable specimens of *Calamostachys* were recorded. In one of the sections figured (pl. 15, fig. 15) the carinal or fascicular canals, so characteristic of Equisetaceous plants, are distinctly shown in the axis of the strobilus, but their significance was overlooked.

In the next year (mem. xi., 1880) a most important discovery—that of a heterosporous *Calamostachys*—was recorded. This form was at first referred to the original species, *C. Binneyana*, though subsequently shown to be specifically distinct. The author said: "This discovery

only strengthens my old conviction that the true affinities of the strobilus are with the Lycopodiaceæ". Yet a figure in the same memoir shows in the most striking way the resemblance of the peltate scales to those of *Equisetum*.

In 1887 the memoir appeared "On the True Fructification of *Calamites*" (xiv.). The strobilus described here is the same as that recorded in 1870 (xxiii.), but in the meantime several fresh specimens had been discovered, and the structure worked out in the most painstaking manner. The importance of this work consists in the fact that a fructification with axillary sporangiophores (*Palaostachya* of Weiss) was proved to be borne on a peduncle with the exact structure of a Calamitean stem. Williamson regarded this as the only fructification hitherto discovered, which had any claim to be regarded as that of a Calamite.

In 1888 (mem. xv.) Williamson recognised for the first time, though in somewhat guarded language, the existence of a pith in the axis of *Calamostachys*, and so gave up the one basis for his old position. In the same memoir he gives the finest figure of the peltate scales which has ever been published, and points out that they "approach even more nearly than they were previously known to do, to those of the living *Equisetums*". At this time he said nothing more definite as to affinities, but in his Index, part i., 1891 (25\*) *Calamostachys* found its proper place at last in the family Calamariæ.

In a paper published at Manchester in 1886 (25), a useful and very clear comparative account of the anatomy of the three genera, *Calamites*, *Calamopitys*, and *Calamodendron*, is contained.

The present writer does not think it necessary to make any detailed reference to the later memoir, in which he himself co-operated (29). A statement of the present position of our knowledge of *Calamites* will be found in Mr. Seward's article (43). Enough has been said to show in how large a degree this knowledge has been acquired through Williamson's labours.

The *Calamites* are a group the affinities of which may

now be considered as fairly well established. This is not the case with the family of the *Sphenophylleæ*, which we will take next in our survey of Williamson's work. This group is entirely unrepresented in the recent Flora, and its existence has only been revealed by palæontological research.

Our knowledge of these remarkable plants is chiefly due to two men—Renault and Williamson.

In the fifth memoir of the *Phil. Trans. Series* (1873) the latter author gave an admirable account of the structure of two species of *Sphenophyllum*, which he at that time described under the name of *Asterophyllites*. The form of the leaves in Williamson's Oldham specimens did not agree with the definition of the genus *Sphenophyllum* as then understood. We now know that the foliar characters have a very wide range of variation in *Sphenophyllum*, and Williamson's specimens are now placed without hesitation in that genus. In memoir v. all the main features of the anatomy were already described; the secondary growth was at once rightly interpreted by Williamson, though its recognition as such was long evaded by his French fellow-worker, in consequence of the invincible prejudice entertained by Brongniart's pupil against the possibility of cambial growth in a Cryptogam.

As to one of the two species investigated by Williamson (that now known as *S. plurifoliatum*) there has never been any doubt. The other, however (*S. insigne*), includes some unusually large specimens, with a very root-like transverse section, and showing some slight differences from the typical forms. Several of the chief authorities, such as Renault, Schenk, and Solms-Laubach, refused to recognise these larger specimens as *Sphenophyllum* or anything of the kind, and supposed them to be roots of some unknown plant. It turns out, however, that Williamson was perfectly right. The discovery of *Sphenophyllum* leaves on specimens manifestly identical with the disputed forms has settled the question, and the most formidable of the former opponents, Solms-Laubach, has now announced his conversion to Williamson's opinion (45, p. 247). The correctness of our author's

identification depended partly upon his sound estimate of the anatomical characters involved, and partly on his fine series of specimens.

Our knowledge of the fructification of *Sphenophyllum* is primarily due to Williamson, without whose researches we should have no idea of its real structure. As early as 1871 he published a paper on "*Volkmannia Dawsoni*, an Undescribed Verticillate Strobilus from the Lower Coal-Measures of Lancashire" (24), and already expressed the opinion that "it is the fruit either of *Asterophyllites* or of *Sphenophyllum*" (p. 37). In memoir v. of the series in the *Philosophical Transactions*, a fuller description of the cone was given, in memoir xvii. (1890) the discovery of its vegetative stem was announced, and lastly, in the following year (mem. xvii.) a number of new specimens were described, and all essential points in their organisation explained. The strobilus consists of an axis bearing many whorls of coherent bracts, from the upper surface of which the numerous sporangiophores arise; each of the latter is of considerable length, and bears a single pendulous sporangium at its apex. Up to this time the fossil was placed in Binney's genus *Bowmanites*, but its affinity to *Sphenophyllum* was always recognised by its discoverer. The full description of the structure given by Williamson enabled Zeiller in 1892 (46) to identify the fructification of the well-known *Sphenophyllum cuneifolium* as being of essentially the same nature, and thus to determine for the first time the true character of the fruit in that genus.

The organisation of *Sphenophyllum* is now as thoroughly known as that of a genus of recent plants, and few fossils have such indisputable claims to autonomy. The idea which still sometimes finds expression, that *Sphenophyllum* may represent the foliage of a Calamite, is due to a confusion of thought. Certain forms of foliage in some species of *Sphenophyllum* may doubtless bear an external resemblance to some forms of Calamitean foliage, but the genus *Sphenophyllum* is characterised by its structure and fructification, and not merely by the form of the leaf.

In his later works Williamson placed *Sphenophyllum* in the family Calamariæ, following Weiss in this, but he fully recognised that their systematic position is still an open question. A remarkable, newly discovered fructification, lately described by Solms-Laubach under the name of *Bowmanites Römeri*, appears likely to throw some further light on the affinities of the group (45).

The next family which we propose to consider in illustration of Williamson's work, is one of which he may fairly be called the discoverer. This is the group *Lyginodendrea*. Although a few specimens had been previously observed, the investigation and interpretation of their structure has been practically in our author's own hands. The first full account of the genera *Lyginodendron* and *Heterangium* occupies the fourth memoir of the series in the *Philosophical Transactions*. At this time the main points of the anatomy of the stem in both genera were determined. Williamson, with his usual acumen in such matters, at once saw that the two plants were closely related, though there is a striking difference between them, *Lyginodendron*, at least in the normal form, having a large pith with a ring of distinct bundles around it, while in *Heterangium* the wood extends to the centre, and there is no pith at all. At that time Williamson already suspected that the leaves which he then called *Edraxyton* belonged to *Lyginodendron*, and "then," he said, "strange as it may appear, *Lyginodendron* will become an undoubted arborescent Fern". This conclusion may well have appeared strange, for the anatomy of the stem of *Lyginodendron* is much like that of a Cycad, especially as regards its secondary tissues.

Restorations of the stems of both genera are figured in the memoir of 1872. They are extraordinarily good, that of *Heterangium* especially being so exact that it could not be improved upon at the present day after all the additional work that has been done.

The foliage was fully described in 1874 (mem. vi.) under the name of *Rachiopteris aspera*, and shown to be of the *Sphenopteris* type. The proof that it really belonged to *Lyginodendron* was, however, reserved for a much later



memoir (xvii., 1890), and has been finally confirmed by still more recent researches.

In the meantime (in mem. vii., 1875, and mem. xiii., 1887) a beautifully preserved fossil had been described in great detail under the name of *Kaloxylon Hookeri*. It was then looked upon as a distinct plant, though its discoverer recognised the similarity of its tissues to those of *Lyginodendron*. More recent investigation has proved that *Kaloxylon* is nothing else but the root of *Lyginodendron* (31).

In 1887 a second species of *Heterangium*, remarkable for the extraordinary development of its secondary phloëm, and for the exceptional perfection with which its tissues are preserved, was described. In this memoir Williamson speaks of *Lyginodendron* and *Heterangium* as being "possibly the generalised ancestors of both Ferns and Cycads," a view which, in the light of our present more complete knowledge, appears to come near the truth.

The proof of the existence of this intermediate group was certainly a discovery of the first magnitude, the importance of which, though ignored in this country, was fully recognised on the Continent.

It cannot be denied that in this and one or two other instances the great merit of Williamson's work was somewhat obscured by the prominence which he gave to certain mistaken ideas as to development. He was always disposed to interpret specimens of the same plant which differed in size and structure, as being necessarily developmental stages of one and the same organ, whereas such differences are just as often due to the order of the branch or to the level at which the section happens to be taken. Consequently when he found some specimens of a stem with little or no pith, and others with a large one, he thought it necessary to explain how the former developed into the latter, and this led to his theory of the development of the pith from "primitive cells which lurked among the vessels," and to further hypotheses which appeared to other botanists to involve mechanical impossibilities. In the special case of *Lyginodendron* the matter was further complicated by the fact that roots were not always distinguished from small

stems. This questionable theory no doubt produced a certain prejudice in the minds of botanists against work which in all other respects was excellent.

Just before the close of his life, Williamson, with a rare openness of mind, convinced himself that these views were mistaken.

The fourth group which we propose to deal with is that of the Lycopodiaceous plants. It is more difficult here than in previous cases to give in a few words any idea of what was accomplished, for the forms investigated are numerous, and a general survey of the present state of our knowledge has still to be made. As is well known, Brongniart had taken the same course with this group as with the Calamariæ. The specimens of *Lepidodendron* which he examined (*L. Harcourtii*) happened to be without secondary tissues, while his *Sigillaria* of course possessed them to a conspicuous extent. Brongniart saw the distinction quite clearly (for he was a good anatomist for that day as well as a great systematic botanist), and attached so much importance to it that he placed *Sigillaria* among Phanerogams, while leaving *Lepidodendron* in Lycopodiaceæ. Williamson in his memoir ii. (1871), the first which treats of these plants, at once attacked the position of the French palæontologist. He says: "I am now in a position to demonstrate the complete unity of the plants which M. Brongniart has separated so widely, and to show that the transition from one form to another is so gradual as to necessitate the inclusion of the entire series in the Lepidodendroid family". Ultimately he completely justified his contention, and, with perhaps one exception, brought round all his opponents to his opinion.

The earlier memoirs on Lycopodiaceæ have two drawbacks. First, that the author applied the terminology proper to Dicotyledons not only to the *secondary* tissues (where such an application is justifiable) but also to the primary structure, which in Lycopodiaceous plants is of course quite peculiar. Secondly, he attached too much systematic importance to the occurrence of secondary growth, and even proposed a classification of vascular Cryptogams based on

this character. Both these defects, however, are limited to the earliest papers of the series, while from first to last Williamson's account of the actual anatomical facts was in all essentials correct.

It would take too long to follow in any detail the progress of our author's work on the fossil Lycopodiaceæ. No less than eight of the Royal Society memoirs are devoted wholly or in part to these plants, besides which there are three other treatises, namely, an important controversial paper which appeared in the *Annales des Sciences Naturelles* for 1882 (28), the great monograph on *Stigmaria ficoides* (27), 1887, and the last paper he ever wrote, that on the mode of growth of the *Lepidodendra*, which only appeared this year (26). The unrivalled wealth of material in Williamson's possession, with which he was constantly supplied by a band of enthusiastic fellow-workers, enabled him to place our knowledge of the structure of Lepidodendreae on an exceedingly broad basis. The anatomy of ten different forms is described in his memoirs, most of which are known by their leaves to be certainly true *Lepidodendra*, or to belong to the closely allied genus *Lepidophloios*. In six out of the ten the occurrence of secondary thickening of the vascular cylinder (in addition to an enormous development of periderm) has been proved. The only form which attains any considerable size without developing secondary wood is *L. Harcourtii*, the species which originally came into Brongniart's hands, and unfortunately led him to his hasty generalisation. It is a fact of special interest that Williamson's *L. fuliginosum*, a form so similar to *L. Harcourtii* that it was for many years described under the same name, develops at a rather late stage a well-marked secondary zone.

Specimens of *Sigillaria* showing structure are rare compared with those of *Lepidodendron*; Williamson, however, was able to show that there is no essential anatomical difference between Lepidodendroid and Sigillarian stems. This established a strong presumption that, as the *Lepidodendra* are undoubtedly Lycopodiaceous Cryptogams, the same holds good for *Sigillaria*. This presumption became

a certainty, when, in 1884, Zeiller discovered the macrospores of a *Sigillaria* (47). Renault appears to be the only authority who still believes in the existence of Phanerogamic *Sigillariæ*. He continues to regard the *Sigillariæ leiodermae* as Gymnosperms, while acknowledging the Cryptogamic nature of the subgenus *Rhytidolepis*, in which the existence of macrospores has been proved. He considers the whole group as a transitional one, but for this view, however interesting, there appears to be no evidence. All that we actually know tends to show that *Sigillaria*, as a whole, is a Lycopodiaceous genus with the closest affinities to *Lepidodendron*.

Among the fructifications of *Lepidodendron* described by Williamson several afford excellent examples of heterospory. The strobilus of *L. Spenceri* is especially remarkable, the spores (which from their size would appear to be macrospores) being most curiously winged. This plant presents several peculiarities, and it seems probable that, as its discoverer suggested, it may turn out to be generically distinct.

Some of the most important parts of Williamson's work on *Lepidodendreae* relate to the forms known as *Halonía* and *Ulodendron*. He produced evidence which seems to leave no doubt that these stems, formerly regarded as belonging to distinct genera, are nothing but the fruit-bearing branches of *Lepidodendron* or *Lepidophloios*, the tubercles or scars marking the insertion of the fallen cones (see especially mem. xix.).

As regards the subterranean parts of the fossil Lycopods, Williamson did more than any other observer to make their structure known. His monograph on *Stigmária ficoides* (27) has been regarded by competent critics as his best work. Concerning the actual structure little remains to be done, but the morphology of the organs in question is still disputed. That *Stigmária* represents the underground portion of various species of *Sigillaria* and *Lepidodendron*, as first discovered by Binney and Richard Brown, may now be regarded as certain. Williamson always maintained that the stout main axes of *Stigmária*, which branch dichotomously,

are the roots, and the appendages which they bear, the root-lets. This has been questioned by various authors, who interpret the main axis as a rhizome, and the appendages, or at least some of them, as modified leaves. The question is a difficult one, more especially when we consider that in recent Lycopods the differentiation between stem and root is scarcely so sharp as in other vascular plants. Although the principal Stigmarian axes differ very widely both in anatomy and morphology from any known roots, yet the resemblance of their appendages to the monarch roots of *Isoëtes* or *Selaginella* is certainly very striking, and it is by no means improbable that Williamson's interpretation of their homologies may turn out to be the right one.

In the long controversy as to the secondary formation of tissues by means of a cambium in Vascular Cryptogams, Williamson had most English and German palæobotanists on his side. The brunt of the battle, however, was borne by him, and to him the honours of victory are due. How complete this victory was may be shown by the opinions expressed by two leaders of the French school, both of whom were among his former opponents. Grand'Eury expresses himself as follows (48, p. 195): "In any case the opinion that the *Sigillariæ* and *Calamodendra* are Gymnosperms sees from day to day the number of its adherents diminish. At the end of my studies in Le Gard I have been led to consider them as highly organised Cryptogams."

Zeiller, in a letter to Williamson, dated 24th March, 1895, says: "I now at last think the question as to placing the 'Calamodendreae' among the Cryptogams definitely settled. . . . Your work (29) enables me at last to assert without any reserve the Cryptogamic nature of all this group, as regards which I had thought it right until now to mention the opinions of Brongniart and Renault, though strongly opposing them."

This relates to the Calamariæ; as regards the Sigillariæ Zeiller had convinced himself long before. An interesting incident of the controversy when at its height was the publication by Williamson and Hartog of a controversial memoir on *Sigillaria* and *Lepidodendron*, written in the French lan-

guage and published in the *Annales des Sciences Naturelles*, 1882 (28), "a bomb thrown into the enemy's camp," as Williamson was fond of calling it. This paper certainly produced its effect, though it was not till a little later that conviction was brought home to most of the opponents. Ultimately our author was fully justified in saying as he does in his autobiographical notes: "The contest, so far as this great question of the existence of an active cambium-zone producing secondary wood in the stems of Cryptogams is concerned, was settled for ever".

No one who has studied the anatomy of carboniferous plants at first hand can fail to be struck, not so much by the mere occurrence of secondary growth in these ancient Cryptogams as by the close resemblance of the process, in most cases, to that which goes on in normal Gymnosperms and Dicotyledons. This is a remarkable fact, for we know that secondary growth may also take place in totally different ways, as in certain Monocotyledons.

We may be allowed to quote a few words from Count Solms-Laubach's obituary notice of Williamson in *Nature* (32), which places the importance of his results in a clear light: "It was thus made evident by Williamson that cambial growth in thickness is a character which has appeared repeatedly in the most various families of the vegetable kingdom, and was by no means acquired for the first time by the Phanerogamic stock. This is a general botanical result of the greatest importance and the widest bearing. In this conclusion Palæontology has, for the first time, spoken the decisive word in a purely botanical question."

Williamson's last paper on the *Lepidodendrea* (26) has a somewhat melancholy interest. It cost him a vast amount of labour, quite at the close of his life, when he should rather have been enjoying his well-earned rest. His toil, however, was not thrown away, for by means of it he at last convinced himself that his long-cherished views as to the growth of the medulla and primary wood were mistaken. After giving the full details of his elaborate numerations and measurements, he says (p. 59): "Anyhow, it is obvious that my original hypothesis of an enlargement of the

Primary Xylem proceeding from above downwards, is incapable of explaining the facts recorded in the preceding pages. Hence, that explanation appears more likely to be found in some modification of the views of Graf Solms." He goes on to point out, with perfect justice, that certain difficulties still remain.

It requires a very noble spirit of self-abnegation for a scientific man, at the age of seventy-eight, thus to sacrifice to the cause of truth opinions which he had upheld for so long.

We have only touched on certain parts of Williamson's work, and have left an immense number of his investigations altogether unnoticed. It seemed best however to make a selection, and to choose as illustrations the four great types of Vascular Cryptogams on which his most striking results were obtained.

Some apology is perhaps due for the very slight reference which has been made to the work of other palæobotanists. This article relates merely to Williamson's own researches, and it would have been impossible, without extending it beyond all reasonable limits, to include any adequate account of the share of other observers in building up the present fabric of our knowledge.

We cannot conclude this sketch of Williamson's work on carboniferous plants without some allusion to his remarkable powers as a draughtsman—powers which most of us must be content to admire without emulating. Almost all the illustrations to his numerous papers, and in fact all those which relate to anatomical structure, are by his own hand. It is hard to understand how so busy a man can have found the mere time for such minute and detailed labour, but the character of the work (to which full justice is not always done in the published reproductions) bears witness, not only to his marvellous industry, but to rare artistic skill.

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## MINERAL TRANSFORMATIONS.

**A**MONG the most interesting problems which present themselves to the mineralogist are those relating to the "Life-history" of minerals, if such an expression may be used to include their mode of origin, the changes to which they are liable and their decay.

Few minerals are able to resist the transforming influences which operate in the crust of the earth; the changes of temperature and pressure, contact with air, water and the liquids and gases which they contain, together with the slow but continued action of permeating solutions and of electrolytic processes. Apart from the constituents of certain deep-seated and comparatively unaltered igneous rocks, there are few, if any, minerals which have not resulted from the change, decay, or destruction of pre-existing minerals, and, conversely, few exist which are not destined in due course to beget by their disintegration certain other minerals. The history of their transformations possesses, therefore, a double interest, both as indicating the probable nature and order of the chemical and physical processes to which they have been subjected, and as a clue to the nature and constitution of the minerals themselves. To geologists and mineralogists they are for these reasons equally attractive subjects for study.

The problems involved are beset with peculiar difficulties; the initial conditions under which most minerals were formed are hard to realise and impossible to reproduce; the processes to which they have been subjected have operated for such long periods that experimental evidence can rarely be used for comparison.

Again, though it may be certain that a given mineral is the result of alteration, the greatest uncertainty often prevails as to the nature of the original substance, and, further, in many instances where the nature of the initial mineral is beyond doubt, its decomposition products may appear to be ill-defined mixtures which it is hopeless to identify with any known species.

For these reasons the subject of mineral transformations has been an exceedingly fruitful one for speculation, with the inevitable result that what was originally a mere guess has often become stereotyped into a positive assertion, and is accepted without question or criticism.

In one class of mineral substances alone are we on fairly sure ground.

Possessing a certain individuality, a crystallised mineral may under some conditions, although partially changed, retain sufficient characteristics for its identification; in the remarkable class of products known as "pseudomorphs," the identification is often possible even when the original mineral has been entirely converted into something different.

A mineral which is stable under one set of conditions, is frequently unstable under others; when exposed to the action of air, water, or various solvents it may be converted into new substances, and if the action has been sufficiently gradual, the resulting product may preserve intact the crystalline form of the mineral from which it originated. In such a case there can be absolutely no doubt that it was produced by the alteration of that particular mineral, and although the mode of its production may be doubtful, its origin is certain.

Such perfect pseudomorphs, for example, as those found at Wunsiedel in Bavaria, which, while consisting of pure Steatite, present the characteristic and unmistakable form of Quartz, can obviously have resulted only from the alteration or destruction of Quartz crystals. Hence the special and unique interest of such "pseudomorphs," which are, in fact, the only safe guide to a study of mineral transformations.

There are, of course, two possibilities to be kept in view; such pseudomorphs may have been produced by the alteration of the parent mineral, or they may be mere casts of the same. In the latter case we can only conclude that the original crystal has been removed by the action of some solvent, and that its place has been filled by the deposition of new material. Such replacements need not necessarily throw any light upon the constitution either of the initial substance or of the resulting product. Many, possibly the

majority, of the known pseudomorphs have originated in this way.

But there are others which can only have been produced by the gradual alteration of one mineral into another. It may be, for example, that a crystal is found having the characteristic form of Garnet, which consists at one end of unaltered garnet substance, while at the other it has been wholly converted into Epidote. Such a pseudomorph possesses the greatest interest; it not only raises the inquiry what radicles have been removed, what radicles have been introduced during the change, and by what agencies the transformation has been effected; but further it cannot fail to provoke some theory of the composition both of the initial and final compounds.

The complication of pseudomorphous products is not so great as might be expected. That among the varied conditions under which they have originated the total number of known minerals should be so small is always surprising; but that the apparently obscure products and mixtures into which they decompose prove on careful study to be identical with one or other of these well-established compounds is perhaps still more remarkable. Much of the material of pseudomorphs was formerly referred dubiously to mixtures of certain ill-defined species—clays and other hydrated silicates for example; it was scarcely possible to determine their nature by analysis, for it was uncertain how many different minerals they contained.

But since the introduction of microscopical methods there is no longer any excuse for such an evasion; the optical characters of the transparent minerals have mostly been determined, and it is possible to identify them in the minutest crystals.

The use of the microscope has consequently corrected many mistakes which were made by the early mineralogists in their determinations of pseudomorphous materials, and has revealed many new transformations.

Although recent study has done much to clear up the doubts which formerly prevailed regarding the nature of the resulting mineral, it cannot be said that there is the

same certainty about the original minerals from which pseudomorphs were derived. In far too many instances the wildest and most diverse views have been held about the initial composition of the crystals, sometimes owing to the fact that very similar, though not the same, forms may be characteristic of several different minerals.

Pseudomorphs of lead carbonate having precisely the common form of barium sulphate have been found at several localities, and have generally been called pseudomorphs of Cerussite after Barytes; it is obviously far more reasonable to suppose that they were derived not from barium, but from lead sulphate which is isomorphous with Barytes, and therefore has almost the same form, and that the pseudomorphs are really after Anglesite. Again, the Serpentine found at Brewster in New York, which presents a most perfect cubic cleavage, was referred to various cubic minerals which bear absolutely no relation to Serpentine, until Tschermak made the extremely probable suggestion that they are due to the alteration of Periclase, the cubic oxide of magnesium. That Periclase is elsewhere only found in minute crystals is no argument against such an explanation. A similar objection was raised to the idea that the altered tetrahedral crystals found on the River Achtaragda in Siberia, and known as Aechtaragdite, might have been derived from the rare mineral Helvite which they resemble in form; yet crystals of Helvite quite as large as any of the Achtaragdite crystals were subsequently found at two or more localities.

Again, carbonate of lime is sometimes found in acute pyramidal crystals, under such conditions that it might reasonably be supposed pseudomorphous after Celestine; until a recent date this seemed an unlikely explanation, for Celestine was not known to occur in such forms; yet there is clearly no reason why the mineral should not grow in pyramidal crystals, provided that they have angles characteristic of Celestine, and it has recently been found at several localities in acute forms very similar to those of the pseudomorphs.

These are only a few examples out of many which might

be cited to illustrate the doubt which often prevails as to the original source of pseudomorphs.

The process by which they have been produced is often even more uncertain ; and yet those who have attempted a systematic treatment of pseudomorphs have usually devoted their attention mainly to the processes by which they may have been formed, with the object of elucidating the problems of chemical geology.

The two best known and most exhaustive treatises on the subject are the elaborate work of Blum, *Die Pseudomorphosen des Mineralreichs*, 1843 (with four appendices, 1847-1879), and the first volume of Roth's *Allgemeine und Chemische Geologie*, 1879, in which all the previously described pseudomorphs are collected and classified.

Thus in the classification of Blum, they are considered according to the relation between the initial and final substance as due (1) to loss of constituents, as when Gypsum is converted into Anhydrite by dehydration ; (2) to gain of constituents, as when Anhydrite is converted into Gypsum by hydration ; (3) to exchange of constituents, as when barium carbonate is converted into sulphate ; and (4) to total replacement of one substance by another.

In the classification of Roth, a distinction is drawn between those which are due to the simple and direct action of air, water and carbon dioxide, and those which result from the action of solutions containing mineral matter.

In the present state of our knowledge there is here necessarily much that is mere speculation, since, even if the initial and final products are certain, the intermediate steps and processes are rarely known to us.

Taking these and similar difficulties into account, it is clearly necessary in any arguments based upon pseudomorphs to select only those cases in which there is absolutely no doubt as to the nature of the original mineral. A complete revision of the work of Blum and Roth is sorely needed, if only to correct downright errors and to weed the doubtful from the certain.

In no application of such arguments is this more necessary than in those speculations with which the present



article is more especially concerned, namely, the inferences drawn from pseudomorphs as to the chemical constitution of minerals.

It is a curious fact that, disregarding those which are obviously mere casts or moulds, and therefore represent no necessary chemical relations, the true alteration pseudomorphs (metasomatic products) in which one mineral has been gradually transformed into another are few and simple.

If well proved and indubitable cases alone are examined it will be found that any given mineral usually alters into only a few definite compounds, and that any given compound is found pseudomorphous only after a few definite minerals. It becomes, therefore, important to consider whether there be not some relationship between the initial and final product independently of the mode in which the pseudomorph has been produced, and whether there may not be some community of composition between those minerals which result in the same product.

Chemical analysis of the natural silicates explains, as a rule, nothing but their percentage composition, and any attempt to understand their constitution more fully is necessarily based upon highly speculative reasoning. For a long time the only clue available was that afforded by the mutual replacement of one radicle by another in different samples of the same mineral, or in closely allied minerals belonging to the same isomorphous group.

In a recent memoir upon the constitution of the Silicates (*Bulletin of the United States Geological Survey*, No. 125, 1895), F. W. Clarke points out that the mineralogist does not, like the organic chemist, deal with bodies of known molecular weight which can be measured by the density of a vapour or by cryoscopic methods; consequently the only means available are: (1) isomorphism, which indicates similarity of chemical structure; (2) dissimilarity of form with identity of composition, *e.g.*, in Andalusite and Kyanite, which must be taken to indicate isomerism; (3) pseudomorphs; (4) the artificial production of alterations in the laboratory; (5) the thermal decomposition of silicates; (6) their artificial synthesis.

In the alterations of minerals "atoms or groups of atoms can be split off from a molecule and replaced by others, and the information so gained bears directly upon the question of chemical structure".

At the present time such evidence is being actively sought among the various products derived from minerals, either by the processes of nature or by experiments in the laboratory.

The experimental inquiry is one from which much may be expected, but too little has yet been done in this direction. The suggestive experiments of Lemberg, Doelter and others, are of the greatest importance, but cannot be adequately summarised in the present article. But the natural pseudomorphs, if due care be taken, as indicated above, to select only those which are beyond doubt, supply examples which can never be equalled by artificial means.

In Clarke's elaborate memoir frequent use is made of this line of reasoning, and several other papers have been recently published in which the transformations disclosed by natural pseudomorphs are made the basis of a theory of chemical constitution, on the following principle: we may conceive, it is argued, that while a silicate undergoes change, certain radicles constitute a comparatively stable kernel which persists as such, and unites with the incoming radicles.

Among the most familiar materials of silicate pseudomorphs are Kaolin, Serpentine, and Talc: they may be taken as simple and typical examples affording arguments as to the structure of certain silicates from which they have been derived.

(1) Kaolin  $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$  (in which the water is all constitutional) results from the decomposition of Orthoclase  $\text{K Al Si}_3\text{O}_8$ .

Scharizer (*Zeitschr. f. Krystallographic*, xxii., p. 369, 1893), who assumes that in the natural metasomatic alteration products the liberated radicles free just sufficient valencies to saturate the water or hydroxyl introduced, supposes the change to be due to the entrance of four hydroxyl radicles which saturate four freed valencies of

aluminium. Kaolin then has the composition  $(\text{HO})_4\text{Al}_2\text{Si}_2\text{O}_5$  and Orthoclase is  $(\text{Si}_2\text{O}_5)(\text{K Si O}_3)_2\text{Al}_2\text{Si}_2\text{O}_5$ , and both may be regarded as salts of dimetasilicic acid  $\text{H}_2\text{Si}_2\text{O}_5$ .

Clarke, on the other hand, is concerned to prove that the natural silicates are all substitution derivatives of normal salts (mostly of orthosilicates); he therefore regards Orthoclase as having the composition  $\text{K}_3\text{Al}_3(\text{Si}_3\text{O}_8)_3$ , *i.e.*, as a normal salt of the trisilicic acid  $\text{H}_4\text{Si}_3\text{O}_8$ . This acid he considers as equivalent to orthosilicic acid  $\text{H}_4\text{Si O}_4$ , and the acid radicles as mutually replaceable. Such a supposition is conveniently invoked to account for the undoubted fact (in accordance with Tschermak's theory of the Felspars), that Albite  $\text{Na Al Si}_3\text{O}_8$  and Anorthite  $\text{Ca Al}_2(\text{Si O}_4)_2$  are isomorphous and mix in all proportions. The relationship between Orthoclase and Kaolin is then shown in Clarke's interpretation by attributing to the latter the formula  $\text{H}_3\text{Al}_2(\text{OH})(\text{Si O}_4)_2$ . Kaolin is in some respects closely allied to the Micas, and Clarke compares its constitution with that of the Lime-Mica, Margarite,  $(\text{Ca H})(\text{Al O})_3\text{Al}(\text{O H})(\text{Si O}_4)_2$ .

Groth, for the sake of simplicity, regards Kaolin as a dimetasilicate in which the two hydrogen atoms of the acid are replaced by two univalent radicles  $\text{Al}(\text{O H})_2$ , and refers Serpentine, Talc, Picrosmine and Pyrophyllite to the same acid as allied minerals.

(2) Talc  $\text{H}_2\text{Mg}_3\text{Si}_4\text{O}_{12}$  is a very common result of the decomposition of magnesian silicates.

The alteration of Enstatite  $\text{Mg Si O}_3$  to Talc suggests to Scharizer that Enstatite has the composition  $\text{Mg}_4(\text{Si O}_3)_4$ , and Talc  $\text{H}_2\text{Mg}_3(\text{Si O}_3)_4$ , so that the change is simply a replacement of Mg by  $\text{H}_2$  in a normal metasilicate. Clarke, reasoning from the fact that upon ignition one-fourth of the silica of Talc is liberated, prefers to regard this mineral as  $\text{Mg}(\text{Si O}_4)\text{Mg}_2(\text{Si}_3\text{O}_8)\text{H}_2$  or  $\text{H}_2(\text{Si O}_4)\text{Mg}_2(\text{Si}_3\text{O}_8)\text{Mg}$ , *i.e.*, as a pseudometasilicate which is to be taken as a compound orthosilicate and trisilicate. Enstatite he would therefore regard as a similar compound orthosilicate and trisilicate  $\text{Mg}_4(\text{Si O}_4)(\text{Si}_3\text{O}_8)$ . Groth had previously suggested that Talc might be a basic dimetasilicate  $\text{Mg}(\text{Mg OH})_2(\text{Si}_2\text{O}_5)_2$ , while Tschermak, in order to show

Its relationship to the Micas, regarded the mineral as a molecular compound  $\text{Mg}_6(\text{Si O}_4)_3 \cdot \text{H}_4\text{Si}_5\text{O}_{12}$ , the two components of which are according to his theory constituents of the Mica group.

(3) Serpentine  $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$  is the almost universal result of the decomposition of Olivine  $\text{Mg}_2\text{Si O}_4$ .

Scharizer regards both these minerals as di-orthosilicates; Olivine is then  $(\text{Mg}_2\text{O})_2\text{Mg}_4(\text{Si}_2\text{O}_7)_2$  and Serpentine  $\text{H}_2(\text{Mg OH})_2\text{Mg}(\text{Si}_2\text{O}_7)$ .

Clarke regards both minerals as orthosilicates: Olivine as  $\text{Mg}_4(\text{Si O}_4)_2$  and Serpentine as  $(\text{Mg OH})\text{H}_3\text{Mg}_2(\text{Si O}_4)_2$ . This formula for Serpentine was suggested by the results of Clarke and Schneider's experiments with dry hydrochloric acid upon the mineral; they found that only one of the three atoms of magnesium is readily extracted, while the remaining two offer greater resistance to the action of the gas.

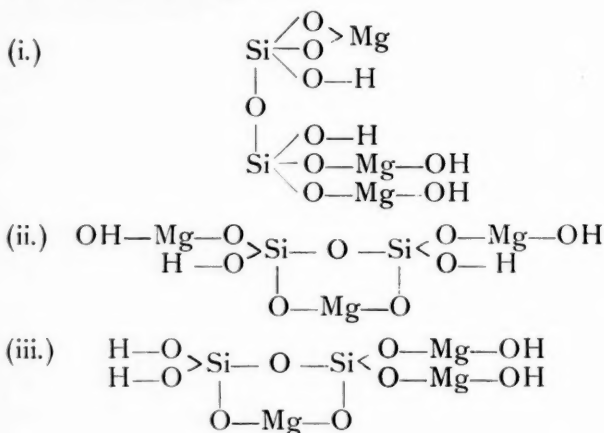
Brauns (*Neues Jahrb. f. Mineralogie* (1), p. 205, 1894) has attributed this difference to the presence of water; this causes the gas at first to act energetically upon the mineral which is then protected by the chloride formed. Experiments made by Lindner have also failed to confirm the results of Clarke and Schneider.

Brauns himself agrees with Scharizer in attributing to Serpentine the formula  $\text{H}_2(\text{Mg OH})_2\text{MgSi}_2\text{O}_7$ , which can be derived by the removal of magnesium and accompanying hydration from  $\text{Mg}_4(\text{Si O}_4)_2$  or Olivine, after passing through an intervening stage in which the composition is  $\text{H}(\text{Mg OH})\text{Mg}_2\text{Si}_2\text{O}_7$ .

Two other facts must be borne in mind in devising a probable formula for Serpentine: firstly, that when it is heated the water is liberated at different temperatures, one molecule going at red-heat, the other at a higher temperature; secondly, that when Serpentine is fused it becomes converted into a mixture of Enstatite,  $\text{Mg Si O}_3$ , and Olivine,  $\text{Mg}_2\text{Si O}_4$ . Both these facts are more or less indicated by the formula just given.

The graphic formulæ used by the above-mentioned authors in support of their various views have not been

reproduced in the preceding pages ; the simplification, or complication, possible in such formulæ may be exemplified by the case of Serpentine ; the structure may here be represented in three ways :—



The first is that adopted by Brauns, the second is that of Tschermak, but the third expresses perhaps even more suggestively the breaking up of the mineral into Enstatite and Olivine. Tschermak prefers the symmetrical grouping (ii.) as harmonising better with the derivation of Serpentine from two molecules of Olivine.

Groth suggests that Serpentine may be one of the two following molecular compounds,  $\text{H}_2\text{Mg}_3(\text{Si O}_4)_2 \cdot \text{H}_2\text{O}$  or  $(\text{Mg OH})_2\text{Si}_2\text{O}_5 \cdot \text{Mg}(\text{OH})_2$ , the former representing a chloritic mineral with one molecule of water of crystallisation, the latter a molecular compound of Picrosmine and Brucite ; but here we begin to lose sight of the relationship to Olivine which is suggested by the pseudomorphs.

I have entered at some length into the views which have been propounded concerning the chemical construction of Serpentine as an instance of the arguments used by these able chemists in their endeavours to solve the mystery of the natural silicates.

Such speculations should perhaps be regarded rather as illustrating the straits to which mineralogists are driven in their study of the silicates than as successful attacks upon

this difficult problem ; they may excite the derision of organic chemists ; but so long as the methods available in organic chemistry have no application in mineralogy, and until other means of exploring the constitution of even the simpler silicates are discovered, we have to make the most of the means at our disposal.

It will be observed that Serpentine and Kaolin have a precisely similar composition, three atoms of magnesium in the one being replaced by two atoms of aluminium in the other. Such common decomposition products deserve special study, since they undoubtedly represent simple substances of an extremely stable nature into which the less stable silicates of the igneous rocks tend to degenerate under ordinary conditions ; no mineral is more stable than Talc ; articles made of Steatite (a compact Talc), though it is so soft a material, have withstood the wear and tear of centuries far more successfully than most materials worked by man ; it is difficult to believe that such minerals do not possess a very simple constitution.

For this reason also we might expect them to present some similarity not only among themselves, but also to those anhydrous minerals (pyroxenes, amphiboles, feldspars) of which they are the hydrated representatives. It is, however, certain that before these relationships can be successfully traced, the natural pseudomorphs need most careful and detailed study in order that their initial and final states, and also the intermediate stages through which they pass, may be definitely established.

H. A. MIERS.

## ON SOME APPLICATIONS OF THE THEORY OF OSMOTIC PRESSURES TO PHYSIO- LOGICAL PROBLEMS.

**I**N a large proportion of the most important functions of the animal body, and especially those classed under the heads of nutrition and secretion, the essential phenomenon consists in a transference of fluid, containing solids in a condition of solution or semi-solution, across a membrane of varying degrees of permeability. It is therefore natural that experiments by chemists on the phenomena of osmosis should have attracted the attention of physiologists and incited them to further investigations on the subject; and we find in the earlier text-books, of which I may especially instance the one by Ludwig, that the subject of osmosis occupies a large section of the work. Until recent years, however, our knowledge of the factors and forces involved in the interchange of substances in solution across animal membranes, was so meagre and inexact that the application of them to physiology could merely serve as a pretext for hazy speculation.

Our first exact knowledge of the forces concerned in osmotic phenomena was furnished by Pfeffer when he measured experimentally the osmotic pressure exerted by various solutions when enclosed in semi-permeable cells. The brilliant generalisations of Van t' Hoff have enabled us to form a correct estimate of the forces involved and of the work done in the osmotic transference of fluid from one side of a membrane to the other, although we do not yet know how it is that these solutions are able to attract water through the cell-wall in order to exert an osmotic pressure equal to that which the molecules of the dissolved substance would exert if in the form of a gas. It was in 1877 that Pfeffer<sup>1</sup> and De Vries<sup>2</sup> published papers on the

<sup>1</sup> *Osmotische Untersuchungen.* Leipzig, 1877.

<sup>2</sup> *Die Mechanischen Ursachen der Zellstreckung.* Leipzig, 1877.



subject of osmotic pressures and cell turgor. Nine years elapsed before the subject was taken up by animal physiologists, and it is only during the last few years that we have awakened to the importance of Pfeffer and Van t' Hoff's researches and their manifold application to our science.

Hamburger<sup>1</sup> was the first, at the instigation of Donders, to apply these results to questions in animal physiology. In his first paper on the subject he confines himself to testing on blood-corpuscles the results obtained by De Vries with plant cells, and found that these corpuscles might be used for demonstrating the isotonicity of equivalent salt solutions. De Vries compared in different salt solutions the concentration at which the plasmolysis first began to take place. Hamburger found that red blood-corpuscles began to lose their hæmoglobin in salt solutions of a certain concentration varying with the nature of the salt. It was thus possible to determine the relative osmotic pressures of two salt solutions by observing how much distilled water must be added to each in order to produce breaking up of the corpuscles and tinging of the fluid by hæmoglobin. Hamburger in this way obtained results much exceeding in accuracy those got by experimenting on vegetable cells. The definiteness of the point at which the breaking up of red corpuscles begins is the more surprising, as Hamburger has shown that the membrane or limiting layer of the red corpuscles is not impermeable or "semi-permeable," in the sense that Traube's membranes are, but that it permits the passage of salts and even of proteids. The transfer, however, of substances from the corpuscles to the surrounding medium is invariably accompanied by a passage of other substances in the medium into the corpuscles, and this exchange always take place in isotonic proportions, so that the tonicity, or osmotic pressure, of the surrounding fluid, as of the red corpuscles, is unchanged. It would be difficult to give any physical explanation of this curious interchange, and Hamburger is evidently inclined to ascribe

<sup>1</sup> *Archiv f. Anat. u. Phys.*, p. 476, 1886, and p. 31, 1887, and other papers.

it to a vital action of the red blood-corpuscles, which merely means that the process is at present inexplicable.

Since the publication of the above paper, Hamburger has published a number of others on the relationships between the blood-corpuscles and plasma, and between the circulating blood and the extravascular lymph. To some of these we shall have occasion to refer later on.

In the meantime publications of Van t' Hoff and of Ostwald have given the impetus to a number of other researches by physiologists on the bearing of osmotic pressures on physiological processes. These researches fall naturally into two main groups.

In the first place, just as we can estimate the work done by a muscle by measuring the load raised and the height to which it is raised during a given time, so we can determine the minimum work done by a secreting cell by measuring the osmotic difference between the secreted fluid and the fluid from which it is formed, *i.e.*, the blood-plasma. Moreover, in many cases we can use a determination of the osmotic pressures in order to judge whether the absorption of a fluid across a given membrane is a simple physical process, dependent on osmotic differences, or whether the fluid moves against pressure, and the absorption must therefore involve the active intervention of the cells forming the membrane. Of works of this class, perhaps one of the most interesting is that by Dreser<sup>1</sup> on the work done in the secretion of urine.

Dreser makes use of the depression of freezing point to determine the osmotic pressures of blood or blood-plasma and urine. Since blood-corpuscles are destroyed in solutions of urea, they cannot be used as an index to the tonicity of this fluid. He points out in the first place that, from Van t' Hoff's results, it is possible to calculate directly the work done in concentrating a solution by the separation of a certain amount of pure water in the form of ice. If  $\Delta$  is the depression of freezing point and  $T$  the absolute freezing point of the solvent (*i.e.*, for water,  $273^{\circ}$ ,

<sup>1</sup> Ueb. Diurese und ihre Beeinflussung durch pharmakologische Mittel, *Arch. f. Exp. Path.*, xxix., p. 307, 1892.

and  $w$  the latent heat of fusion of ice = 79 cal.), then the work can be reckoned from the following formula:—

$$dA = \frac{\Delta w}{T} \times dv.$$

Thus for 1 per cent. solution of cane-sugar ( $\Delta = \cdot 055$ )

$$dA = \frac{\cdot 055 \cdot 79}{273} \times dv.$$

To reduce this result to gravitation units we must multiply by 424, and we thus find that to separate the volume  $dv$  of pure water as ice from 1 per cent. cane-sugar solution, a force is necessary equal to the pressure of a column of water of  $\frac{\cdot 055 \times 79 \times 424}{273}$  metres in height.

A depression of  $\Delta = -1^\circ$  corresponds therefore to an osmotic pressure of  $\frac{79 \times 424}{273}$ ; that is to say, to 122·7 metres of water. We have therefore to multiply  $\Delta$  by 122·7 in order to obtain the osmotic pressure in water of any solution.

We must now consider how these results can be applied to determine the amount of work done by the kidney cells in secreting a given specimen of urine. Dreser takes for an example the case in which during a night 200 c.c. urine were secreted with  $\Delta = -2\cdot3^\circ$ . This was separated by the kidneys from the blood with  $\Delta = -0\cdot56^\circ$ . We have to determine what work has been done in this process. This can be calculated from a simple formula. Let  $a$  be the amount of dissolved substance (a constant). This is dissolved in the variable quantity  $v$ , forming a solution containing  $y$  per cent. We thus get the equation  $\frac{a}{v} = \frac{y}{100}$ ; the concentration  $y$  is, however, also a measure of the osmotic pressure. The amount of work necessary for pressing through a volume of water  $dv$  is therefore  $dA = y \cdot dv$ , or, since  $y = \frac{100a}{v}$ ,  $dA = \frac{100a}{v} dv$ . Therefore  $A = 100a \int \frac{dv}{v} = 100a \log_e v + C$ . If the original quantity of the solvent was  $v_1$ , and the final amount  $v_2$ ,  $A = 100a \int_{v_2}^{v_1} \frac{dv}{v}$  or  $A = 100a (\log_e v_1 - \log_e v_2)$ .

This formula is similar to that for the work done in the compression of a gas at constant temperature. We can now apply this to the special case in which the kidney separated from the blood-plasma with  $\Delta = -0.56^{\circ}\text{C}$ ., 200 c.c. of urine with  $\Delta = 2.3^{\circ}$ .

In order to produce from 100 ccm. of a fluid with  $\Delta = -0.56^{\circ}\text{C}$ ., a fluid with  $\Delta = -2.3^{\circ}\text{C}$ ., the volume of the fluid must be reduced to 24.348 c.c. ( $0.56:24.348::2.3:100$ ). Hence 76.65 c.c. of pure water must be pressed out of every 100 c.c. of the original solution. By replacing these figures in the above formula we get:—

$$\begin{aligned} A &= 100 \times 0.56 (\log_e 100 - \log_e 24.35). \\ &= 100 \times 0.56 (\log_e 100 - \log_e 24.35) \times 2.30258. \\ &= 79.11. \end{aligned}$$

In this act of concentration, however, the 76.65 c.c. water which are pressed out enter a medium, not of pure water, but of lymph and blood with  $\Delta = -0.56^{\circ}\text{C}$ . The osmotic difference therefore which has to be overcome in the concentration is not represented by 2.3, but only by  $2.3 - 0.56^{\circ}\text{C}$ . Hence the work done  $A$  will be not 79.11, but  $79.11 - 75.65 \times 0.56 = 36.75$ .

To reduce this result to gravitation units we must multiply by 122.7 ( $\Delta = -1^{\circ}\text{C}$ . corresponds to 122.7 metres water), and thus find that 4509.5 gram metres work are necessary to produce from 100 c.c. fluid with  $\Delta = -0.56^{\circ}\text{C}$ ., 24.35 c.c. of secretion with  $\Delta = -2.3^{\circ}\text{C}$ . Hence if the kidney has secreted 200 c.c. of urine with  $\Delta = -2.3^{\circ}\text{C}$ ., the work it has performed is represented by  $\frac{200}{24.35} \times 4509.2$  kilogram metres = 37.037 kilogram metres.

Dreser then proceeds to investigate the work done in the secretion of concentrated and dilute urines, and also the effect of diuretics on this work. One interesting result he obtains relates to the maximum force of the kidney. From a cat which had been deprived of water for three days he drew off some urine with  $\Delta = -4.72^{\circ}\text{C}$ . The blood at the same time had an osmotic pressure corresponding to  $\Delta = -0.66^{\circ}\text{C}$ . These figures denote an osmotic difference of 498 metres water, *i.e.*, a pressure of 49,800 grams per

square centimetre. The absolute force of human muscle is 8000 grams, so we see that the mammalian kidney can exert a force six times greater than the maximum performance of voluntary muscle.

Of course these results absolutely disprove Ludwig's old mechanical theory of urinary secretion. According to this theory the urine is formed by a process of filtration from the glomerular blood-vessels. The fluid thus furnished is free from proteid and less concentrated than the blood-plasma. Since a blood pressure of 200 mm. Hg = 2.72 metres water, and  $1^\circ\Delta = 122.7$  metres water, the highest possible difference between dilute urine and blood could only be  $\Delta = 0.022^\circ\text{C}$ . Dreser finds, however, that after beer drinking and in diabetes insipidus the urine secreted may have  $\Delta = 0.16^\circ\text{C}$ ., i.e., a difference between  $\Delta$  of blood and  $\Delta$  of urine of .4. Hence the production of urine by the glomeruli is also attended with the doing of work, and must therefore be looked upon as a process of secretion. Ludwig further considered that the dilute urine was concentrated on its passage through the tubules by the osmotic passage of water into the concentrated blood-plasma. This, however, is also impossible (as Hoppe Seyler showed long ago), since the urine as normally secreted is much more concentrated than the blood-plasma, and the difference may, as mentioned above, attain to enormous amounts ( $\Delta$  of blood =  $-0.56^\circ\text{C}$ . and  $\Delta$  of urine =  $-4.7^\circ\text{C}$ .).

In a paper published a few months ago,<sup>1</sup> Heidenhain applies the same method to deciding the question whether the absorption of salts and water from the intestines depends merely on the osmotic difference between intestinal contents and blood, or whether this act is carried out by the walls of the mucous membrane in opposition to the osmotic differences. In his experiments about 100 ccm. of salt solutions of varying concentration were introduced into a loop of the ileum a little above the iliacæcal valve, and the loop then returned to the abdomen. Half an hour

<sup>1</sup> "Neue Versuche über die Aufsaugung im Dünndarm." *Pflüger's Archiv*, lvi., p. 579.

later the abdomen was reopened, and the loop emptied of all remaining contents, which were analysed.

I will here quote one or two of the experiments as examples of the method employed and the results obtained.

(1) Dog 14.1 kilos. Blood serum :  $\Delta = 0.634$  : NaCl = 0.620 per cent. Introduced 120 c.c. of salt solution containing 0.3 per cent. NaCl, and therefore .36 grams NaCl ( $\Delta = 0.230$ ). Fifteen minutes later the loop only contained 18 c.c. fluid, with 6 per cent. NaCl (*i.e.*, 0.108 grams).

(2) Dog 7 kilos. Blood serum :  $\Delta = .642$ .

(a) At 9h. 6m. injected 80 ccm. NaCl 1.98% = 1.58 gr. NaCl.

At 9h. 26m. found 80 ccm. „ 1.20% = 0.96 „ „

Absorbed in 20 mins. 0 ccm. .62 gr. NaCl.

(b) At 9h. 30m. injected 80 ccm. NaCl 1.98% = 1.58 gr. NaCl.

At 10h. 10m. found 63 ccm. „ 1.10% = 0.69 „ „

Absorbed in 40 mins. 17 ccm. containing 0.89 gr. NaCl.

(c) At 10h. 13m. injected 80 ccm. NaCl 1.98% = 1.58 gr. NaCl.

At 11h. 13m found 42 ccm. „ 0.96% = 0.40 „ „

Absorbed in 60 mins. 38 ccm. containing 1.18 gr. NaCl.

The freezing points of the solutions were :—

Of the 1.98 per cent. solution  $\Delta = 1.243$ .

And of the unabsorbed fluid in (a)  $\Delta = 0.916$ .

(b)  $\Delta = 0.802$ .

(c)  $\Delta = 0.790$ .

It is evident, simply from these two experiments, that the absorption of water and salts from the intestines cannot be due to the osmotic differences between blood and intestinal contents.

In experiment (1) the osmotic differences would give rise to a transfer of water from intestines to blood, and of NaCl from blood to intestines. We find, however, that there is an absorption both of water and of salt.<sup>1</sup>

In experiment (2) the osmotic difference would occasion a flow of water from blood to intestines, and of salt from intestines into the blood stream. Here again, however,

<sup>1</sup> For a possible mechanical explanation of this result, see *Journ. of Phys.*, vol. xviii., p. 113.

the absorption of water from the intestines begins to take place long before the osmotic pressure of the fluid has reached that of the blood, and the lowering of the osmotic pressure takes place in consequence of absorption of salt, and not from a pouring out of water.

From a study of these and many similar experiments Heidenhain concludes that two kinds of processes are at work in intestinal absorption. In the first place, there is the physiological activity of the living cells, which take up probably a fluid of the composition of the intestinal contents; and, in the second place, there is the purely physical force of osmosis, which, according to the composition, may aid or subtract from the effect of the cellular activity. The result then is due to the algebraic summation of these two distinct processes, the one physical, the other physiological.

The physiological factor can be annulled by mixing with the salt solutions minute traces of a poison such as sodium fluoride. By this means the cells are paralysed, or hindered in their activities, and the absorption of water or salt now takes place in the direction determined by the osmotic differences. Magnesium sulphate appears to have a somewhat similar action, but to a much less marked degree.

Hamburger<sup>1</sup> has employed a somewhat similar argument to prove that lymph cannot be produced by a process of filtration, and that in its production work is done by the endothelial cells of the capillaries. I have pointed out elsewhere<sup>2</sup> several evident objections to his reasoning, and experiments of my own have shown me that the sooner the lymph is tested after it has left the vessels the closer is its osmotic pressure to that of the blood-plasma, and that the minute difference in osmotic pressures ordinarily observed between blood and lymph is due to the fact that this latter alters the tissue cells in its way to the lymphatics,

<sup>1</sup> "Untersuchungen über die Lymphbildung." *Zeitsch. f. Biologie*, p. 143, 1893.

<sup>2</sup> "The Influence of Mechanical Factors on Lymph Formation." *Journ. of Phys.*, xvi., p. 266.



and has its osmotic pressure raised by the waste products of the cellular metabolism.

These few examples will serve to show the many possible applications of the theory of osmotic pressures in determining the work done in the chemical functions of the body. It seems to me probable, however, that the theory may be of yet wider application. In the paper above quoted Heidenhain, after comparing the living cell to a steamer which may, and often does, float down with the stream, but can, under circumstances, move up against the stream, points out that our knowledge of the structure of this mechanism is so imperfect and restricted by instrumental shortcomings that physiologists cannot at present attempt to say how a given force is evolved in the cell, but must confine themselves to locating the exact seat of the energies in the body. I think this is perhaps rather too pessimistic a view to take of our possibilities. Secretion-pressure, movement, are among the phenomena regarded as essentially vital, and yet the botanist will explain root-pressure, movement, as consequences of changing osmotic pressures. We know already that every manifestation of activity is associated with katabolic changes, that is, a breaking down of large unstable molecules into smaller and more stable molecules, so that, wherever these changes are going on, there must be a rise of osmotic pressure. All we want is a suitable mechanism to direct the process, and it is possible that we may explain muscular work, secretion-pressure as directly due to these changes in osmotic pressure.

The possibility of such an explanation seems to have struck several observers, but, so far as I am aware, no serious attempt has yet been made to place an explanation along these lines on a firm experimental basis.

ERNEST STARLING.

## THEORIES OF ELECTROLYSIS.

OUR knowledge of the phenomena which accompany the passage of currents of electricity through liquids has lately been much extended, and our theoretical ideas about the nature of electrolytes have undergone at least an equal development.

At the present moment it seems worth while to state the actual condition of the subject, and to trace the line between ascertained facts and the necessary consequences of those facts on the one hand, and the hypotheses which have been framed in order to explain them on the other.

The fundamental phenomenon from which we shall start is the truth of Ohm's law for electrolytes. This is an indirect deduction from the work which has been done by Kohlrausch and others on the measurement of the conductivity of liquids, and the accuracy with which the law holds has been investigated by Fitzgerald and Trouton and shown to be very great.

Considering the whole of a circuit containing an electrolytic cell, it is obvious that Ohm's law cannot express the facts, since no current will pass till the reverse electromotive force of polarisation is overcome. But polarisation only exists at the electrodes, and, once the current gets inside the liquid, its intensity is strictly proportional to the effective electromotive force which there acts. It follows that no chemical work can be done by the electrical forces acting within the liquid, so that either interchanges between the parts of the molecules must already be going on, or else the work done in tearing asunder one molecule must be given back by the formation of the next.

Since the former of these hypotheses is supported by the facts of chemical double decomposition, it is generally adopted, and we hence conclude that molecular interchanges are always going on, whether or not a current passes—the effect of the electromotive force being to carry a positively electrified stream of ions in one direction, and a

negatively electrified stream in the other. The parts which the molecules interchange with each other need not, as far as we have seen, remain dissociated for any appreciable time. The chemical properties of electrolytic solutions and their agreement with Ohm's law can be explained by supposing that interchanges between the ions only occur when two molecules collide. According to this view, the ions work their way through the solution by means of a continuous series of molecular decompositions and recompositions—the function of the electromotive force being to make the majority of kations pass to the next molecule on the kathode side, and the majority of anions pass to the next molecule on the anode side. An ion can thus only take a step forward when the molecule of which it forms part meets another molecule.

The most important contribution to the theory of electrolysis since the time of Faraday was made by F. Kohlrausch when he introduced the idea of ionic velocity.<sup>1</sup> He pointed out that the conductivity of a solution—that is, the quantity of electricity which passes in one second through a unit cube of the liquid when opposite faces of the cube are kept at unit difference of potential—must be proportional to the number of ions in unit volume multiplied by the velocity with which they travel past each other under the influence of the electromotive force. This relative velocity of the ions can, therefore, be calculated from measurements of the conductivity of an electrolytic solution. Now the ratio of the opposite ionic velocities can be found by observations on the unequal rate of dilution of the solution round the two electrodes when a current passes, as Hittorf pointed out, so that the absolute velocities of the ions, under unit potential gradient, can be calculated in centimetres per second.

Kohlrausch found that, in very dilute solutions, the conductivity was proportional to the concentration; the ionic velocities must, therefore, in such solutions, be constant.

<sup>1</sup> *Wied. Ann.*, 1879, 6. pp. 1, 145; 1885, 26, p. 161; 1893, 50, p. 385.

Moreover, he showed that the velocity of any one ion—sodium suppose—was independent of the nature of the solution containing it—the same, for example, in a dilute solution of sodium chloride as in one of sodium nitrate. In this way he was able to assign to many ions specific ionic velocities—numbers representing the speeds with which they move through a very dilute solution, when driven by a potential gradient of one volt per centimetre. These results were confirmed in two ways. Kohlrausch calculated the conductivities of various solutions from the velocities of their ions as found by observations on other solutions containing them, and showed that the values thus obtained agreed with those given by direct measurements, and Oliver Lodge and the present writer have directly observed the velocities of various ions, by tracking them through the liquid by means of indicators or changes in colour, and again confirmed Kohlrausch's numbers.

Passing to solutions of greater concentration, Kohlrausch showed that the conductivity increased more slowly than the concentration. If we call the number obtained by dividing the value of the conductivity by the concentration (expressed in gram-equivalents per litre) the molecular conductivity, we can express Kohlrausch's results by saying that, as the concentration of an electrolytic solution decreases, the molecular conductivity gradually rises and tends to a constant limiting value as the dilution becomes infinite.

The decrease in the molecular conductivity indicates a corresponding decrease in the velocities of the ions. It is much greater than can be explained by changes in the ionic viscosity, and must be due to some other cause. We must suppose that, in such solutions, the ions are electrolytically active only for a part of their time, and, during the rest of their existence, they are incapable of moving forward. We shall find other indications, both from chemical and from osmotic pressure phenomena, that, at any instant, a certain number of the molecules differs from the rest in condition, and the same number as we deduce from the conductivity is indicated by these two effects. Various hypotheses might be framed in order to explain the

physical difference between the active and inactive molecules. The most important of these is that due, in the first place, to Arrhenius, who supposes that an electrolytically active molecule is dissociated into its ions. We might, however, as far as we have yet gone, imagine that the necessary condition for electrolytic activity was a certain temporary arrangement of the atoms in the molecule, or that two molecules could interchange their ions only when they collided in a certain definite way. Let us, then, for the present, call the state of activity of a molecule *ionisation*, and not use the word *dissociation*, which commits us to one hypothesis.

It is evident from what has been said, that the ionisation of a solution of a certain strength (*i.e.*, the fractional number of its molecules electrolytically active at any moment) is measured by the ratio of its molecular conductivity to the molecular conductivity of a solution of the same substance at infinite dilution, when all the molecules are active. Thus, if we denote the molecular conductivity by the symbol  $\mu$ , and its value at infinite dilution by  $\mu_{\infty}$ , we get for  $\alpha$ , the coefficient of ionisation, the value  $\mu/\mu_{\infty}$ .

In the year 1883, Arrhenius published a paper<sup>1</sup> in which he showed that this coefficient of ionisation was intimately connected with the chemical activity of the solution, and with the amount by which the osmotic pressure of an electrolytic solution exceeds that given by the solution of a non-conducting substance. The comparison has since been extended by Ostwald and others, and a few of the results are given below in a tabular form.

The subject of chemical affinity has lately been examined in the pages of this magazine by Dr. James Walker, and the idea of a specific coefficient of affinity, expressing a definite chemical property of any given solution, will be familiar to its readers.

In the following table, the first three columns give the constants of affinity of a few acids, measured in different ways: (I.) by observing the volume-changes accompany-

<sup>1</sup> *Mém. à l'Acad. des Sciences de Suède*, 1883. Also *B. A. Report*, p. 357, 1886.

ing actions between acids and bases ; (II.) by allowing the acids to act on calcium oxalate, and determining the amount dissolved ; (III.) by comparing the quickening influence of the acids on the decomposition of methyl acetate into alcohol and acid. Finally, in column IV. the relative electrical conductivities of normal solutions of the acids have been tabulated.

Acid.	I.	II.	III.	IV.
Hydrochloric - - -	100	100	100	100
Nitric - - - -	102	110	92	99.6
Sulphuric - - -	68	67	74	65.1
Formic - - - -	4.0	2.5	1.3	1.7
Acetic - - - -	1.2	1.0	0.3	0.4
Propionic - - -	1.1		0.3	0.3
Monochloracetic - -	7.2	5.1	4.3	4.9
Dichloracetic - - -	34	18	23	25.3
Trichloracetic - -	82	63	68.2	62.3
Malic - - - -	3.0	5.0	1.2	1.3
Tartaric - - - -	5.3	6.3	2.3	2.3
Succinic - - - -	0.1	0.2	0.5	0.6

The striking general agreement of these numbers is enough to show that an intimate relation exists between chemical activity and electrical conductivity.

It is found that the osmotic pressures of solutions of electrolytes are abnormally great when compared with those of solutions of non-conductors. By thermodynamic reasoning it can be shown that there must be a connection between the osmotic pressure and the depression of the freezing point, and the exact relation can be deduced. As more investigations have been made on the freezing points of solutions than on their osmotic pressures, it will be convenient to use the freezing points as the bases of comparison. In the case of solutions of non-electrolytes, it is found that the depression of the freezing point is the same for solutions of chemically equivalent strength, so that the effect must be proportional to the number of molecules, and independent of their nature. In solutions of electrolytes the depression of the freezing point is abnormally great, and it is found that the facts agree with the supposition that each electrolytically active molecule produces an osmotic pressure proportional to the

number of ions into which it can be resolved. Thus the effect of an active molecule of KCl is twice that of an inactive one, and the effect of a molecule of  $\text{H}_2\text{SO}_4$  (which gives two H ions and one  $\text{SO}_4$  ion) is, when in a state of ionisation, three times as great as that of a non-electrolyte. If, then, in a certain solution, we have  $m$  inactive and  $n$  active molecules, each of the latter giving  $k$  ions, the total osmotic pressure will be proportional to  $m + kn$ , whereas, if there were no ionisation, it would be  $m + n$ . Let us call the ratio of the actual to the normal osmotic pressure  $i$ , then

$$i = \frac{m + kn}{m + n} = \frac{m + n + kn - n}{m + n} = 1 + \frac{n}{m + n} (k - 1).$$

But  $\frac{n}{m + n}$  is the fractional number of molecules which is at any moment ionised, *i.e.*, the coefficient of ionisation,  $a$ , or  $\mu/\mu_\infty$ , so that it can be found by conductivity measurements, and we get

$$i = 1 + (k - 1)a.$$

By placing the values of  $i$  thus calculated by the side of those directly observed from the freezing point, we get the following comparison :—<sup>1</sup>

Substance dissolved.	No. of gram-equivalents per litre.	$i$ observed from freezing points.	$i$ calculated from conductivities.	$a$ coefficient of ionisation.
Methyl Alcohol	0.1 0.485 0.97	0.97 0.96 1.00	} 1.00	0
Sodium Chloride	0.117 0.194 0.539	1.93 1.87 1.85		
Potassium Sulphate	0.091 0.455	2.35 2.04		
Acetic Acid	0.135 0.337 0.842	1.05 1.04 1.01	1.01 1.01 1.00	.01 .01 .00

Another method of tracing the connection between the two effects is to compare the coefficient of ionisation calcu-

<sup>1</sup> *Zeits. für physikal. Chemie*, ii., p. 491, 1887.



lated from the depression of the freezing point with its value as found from the conductivity. The following are some of the results given by H. C. Jones :—<sup>1</sup>

Substance.	Concentration in gram-molecules per litre.	Coefficient of ionisation.	
		Kohlrausch's result from conductivity.	Jones' result from freezing point.
Hydrochloric Acid -	0.002	1.00	0.984
	.01	0.989	.958
	.1	0.939	.886
Sulphuric Acid - -	0.003	0.898	0.860
	.005	.854	.838
	.05	.623	.607
Ammonia - - -	0.006	0.166	0.111
	.01	.130	.069
	.05	.061	.038

While the small differences probably indicate that secondary effects will ultimately have to be investigated, the striking general agreement shows that the condition of the molecules which makes them electrolytically active is also the chief cause of the increase in the osmotic pressure and of the existence of chemical activity.

So much seems to follow from the facts of the subject. We must now consider the hypotheses which have been framed in order to explain the physical meaning of ionisation. It is well known that the osmotic pressure of a substance in dilute solution not only obeys all the ordinary gaseous laws, but also has the same numerical value as the pressure which the same amount of substance would exert, in the same volume, were it to exist in the gaseous condition. Whether or not it follows from this that the mechanism of osmotic pressure, like that of gaseous pressure, is due to molecular impacts, is perhaps doubtful. It may be that finely divided matter must necessarily possess such properties, whatever be the ultimate physical explanation. Nevertheless, the agreement of dilute solutions with the

<sup>1</sup> *Zeits. für physikal. Chemie*, xii., p. 639, 1893.

gaseous laws shows that the osmotic pressure effects are proportional to the number, and independent of the nature, of the dissolved molecules. When, then, we find that solutions of electrolytes have abnormally great osmotic pressures of such a magnitude as to be proportional to the number of ions into which the electrolyte can be resolved, it is natural to test if the hypothesis that the substance is dissociated into its ions, in such a manner that the ions become physically independent molecules, cannot express the facts of the case.

That substances which show great chemical stability when solid are largely dissociated when dissolved is, at first sight, rather a startling idea. We must remember, however, that it is precisely those bodies which show the greatest amount of chemical activity in solution, that is to say, most readily exchange their ions with those of other molecules. The fact that a solution of potassium chloride does not show any of the properties of the elements, potassium and chlorine, though it has been urged as an objection, is not a conclusive argument against the theory of dissociation, for the ions are certainly under chemical and electrical conditions very different from those under which the elements exist in their usual forms. Another objection which has been brought forward is that the two ions would diffuse at different rates, and be therefore separable. But, since a definite charge of electricity is associated with each ion, it is obvious that, as soon as an ion got separated, it would leave the rest of the substance oppositely electrified, so that electric forces would be brought into play, tending to draw the ion back, and these would increase as more ions wandered away, till they prevented further diffusion. Still, some separation would occur, and a volume of water, in contact with the solution of an electrolyte, is found to take a potential of the same sign as that of the more diffusible ion, leaving the solution to assume a potential corresponding to that of the less diffusible ion.

Further evidence is given by the behaviour of semi-permeable membranes. A membrane of copper ferrocyanide can be prepared which will allow potassium chloride

in solution to pass through it, but is quite impermeable to barium chloride. Now, on the theory of free ions, some of the chlorine will still pass, since it could do so in the first case, but the electric forces will prevent any considerable separation from taking place. But, if we place some substance like copper nitrate on the other side of the membrane, the chlorine ions, which diffuse in one direction, are replaced by nitric acid ions, which diffuse in the other, and this process will continue till we soon find nitrate mixed with the barium chloride, and chloride mixed with the copper nitrate. The salts cannot have directly reacted with each other, for neither alone can pass through the membrane, but the phenomenon is readily explained on the hypothesis of free ions.

It has been shown by Ostwald and others that the properties of salt solutions (*i.e.*, of electrolytes) are largely additive, that is to say, can be found by superposing the properties of the ions which they contain. Such relations have been traced in the densities, colours, refraction coefficients, optical rotatory powers, surface tensions, viscosities, and thermal capacities.

Even stronger evidence, the weight of which seems not to have been fully recognised, is given by the results of Kohlrausch's measurements of conductivity. He proved that, in very dilute solution, the molecular conductivity was constant, that is, that the conductivity was proportional to the concentration. If we suppose that the ions are free from one another, and move forward under the influence of the electromotive force, this relation naturally follows. But if we reject this hypothesis, we have to suppose that an ion, which is then imagined to be free from an opposite ion only at the instants of collision, can take a step forward only when the molecule of which it forms part meets another molecule. Now the frequency with which such collisions occur is proportional to the square of the concentration, so that the average velocity with which an ion can work its way through the solution must also vary as the square of the concentration. But the conductivity is proportional to the number of ions multiplied by their average velocity, hence

the conductivity must, on this hypothesis, vary as the cube of the concentration.

The ordinary laws of chemical equilibrium have been applied to the case of the dissociation of a substance into its ions.<sup>1</sup> As this application is of fundamental importance, a short investigation must be here introduced. Let  $c$  be the number of molecules which dissociate per second when the number of undissociated molecules in unit volume is unity; then  $c\phi$  is the number when the concentration is  $\phi$ . Re-combination can only occur when two ions meet, and, since the frequency with which this will happen is proportional to the square of the ionic concentration, we shall get for the number of molecules re-formed in one second

$$c'q^2,$$

where  $q$  is the number of dissociated molecules in one cubic centimetre. When there is equilibrium

$$c\phi = c'q^2,$$

If  $\mu$  be the molecular conductivity, and  $\mu_\infty$  its value at infinite dilution, the fractional number of molecules dissociated is  $\mu/\mu_\infty$ , and the number undissociated  $1 - \mu/\mu_\infty$ , so that, if  $v$  is the volume of the solution containing one gram-molecule of the dissolved substance, we get

$$q = \frac{1}{v} \left( \frac{\mu}{\mu_\infty} \right) \text{ and } \phi = \frac{1}{v} \left( 1 - \frac{\mu}{\mu_\infty} \right) \therefore \frac{c}{v} \left( 1 - \frac{\mu}{\mu_\infty} \right) = \frac{c'}{v^2} \cdot \frac{\mu^2}{\mu_\infty^2}$$

$$\therefore \frac{c}{c'} = \frac{\mu^2}{v\mu_\infty^2 \left( 1 - \frac{\mu}{\mu_\infty} \right)} = \frac{\mu^2}{v\mu_\infty (\mu_\infty - \mu)}$$

Let us put  $\mu/\mu_\infty = a$ ; then  $a$ , which we have called the coefficient of ionisation, measures both the molecular conductivity referred to its limiting value as unity, and also the fractional number of molecules dissociated.

The equation then becomes

$$\frac{a^2}{v(1-a)} = \frac{c}{c'} = \text{constant} = k.$$

Thus the value of this expression for solutions of binary electrolytes should be constant, and it has been confirmed by Ostwald and others for an enormous number of weak acids. In the case of solutions of strong acids and salt

<sup>1</sup> Ostwald's *Lehrbuch der Allg. Chemie*.

solutions, however, the value of  $k$  does not keep so satisfactorily constant, and no good explanation of the discrepancy has yet been given.

If we put  $\alpha$  equal to  $\frac{1}{2}$  in the equation, we find for  $k$  a value  $1/2\nu$ . Thus,  $2k$  measures the concentration at which the electrolyte is just half dissociated.

Ostwald considers that this constant,  $k$ , gives the "long-sought numerical value of the chemical affinity," since it depends only on the nature of the substance.

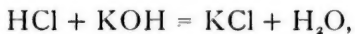
In the case of substances like ammonia and acetic acid, where the dissociation is small,  $1 - \alpha$  is nearly equal to unity, and the equation becomes

$$\frac{\alpha^2}{\nu} = k$$

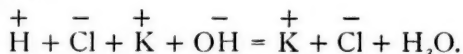
or  $\alpha = \sqrt{\nu k},$

so that the molecular conductivity should be proportional to the square root of the dilution. This result has been fully confirmed by experiments on solutions of acetic acid.

The theory gives an immediate explanation of Hess' law of thermoneutrality, which expresses the fact that, in general, no heat change occurs when two neutral salt solutions are mixed. Since the salts, both before and after mixture, exist mainly as dissociated ions, it is obvious that large thermal effects can only appear when the state of dissociation of the products is very different from that of the reagents. Let us now consider the case of the neutralisation of a base by an acid in the light of the dissociation theory. In dilute solution, such substances as hydrochloric acid and potash are almost completely dissociated, so that, instead of representing the reaction as



we must write



The ions  $\text{K}$  and  $\text{Cl}$  suffer no change, but the hydrogen of the acid and the hydroxyl of the potash unite to form water, which is only very slightly dissociated owing to the fact that, being the solvent, it is present at a great concentration. The heat liberated, then, is almost exclusively that produced by the formation of water from its ions. An exactly similar

process occurs when any strongly dissociated acid acts on any strongly dissociated base, so that, in all such cases, the heat evolution should be approximately the same. This result is fully borne out by the experiments of Thomsen, who found that the heat of neutralisation of one gram-molecule of a strong base, by an equivalent quantity of a strong acid, was nearly constant, and equal to 13,700 or 13,800 calories.

In the case of weaker acids, the dissociation of which is less complete, divergences from this constant will occur, for some of their molecules have to be separated into their ions. For instance, sulphuric acid, which in the fairly strong solutions used by Thomsen is only about half dissociated, gives a higher value for the heat of neutralisation. Since the salts formed are almost completely dissociated, it follows that heat must be evolved when a molecule of sulphuric acid is dissociated into its ions. The heat of formation of a molecule from its ions is, of course, not the same as that associated with the formation of the molecule from its elements in the usual way, for the energy of the ion is very different from that of the atom in its normal state.

If we know the temperature coefficient of dissociation, it is possible to calculate the heat of formation of a gram-molecule from its ions by means of a thermodynamical relation, which was first applied by Clausius to the case of the evaporation of a liquid. In this way Arrhenius<sup>1</sup> has deduced the heats of formation of many bodies, from which the following are selected :—

		Heat of Formation.	
		At 21.5°.	At 35°.
Acetic Acid	-	+ 28	- 386
Propionic Acid	-	- 183	- 557
Phosphoric Acid	-	- 2103	- 2458
Hydrochloric Acid	-		- 1080
Soda	-		- 1292
Potassium Chloride	-		- 362
Sodium Butyrate	-		+ 547

<sup>1</sup> *Zeits. für physikal. Chemie*, iv., p. 96, 1889; ix., p. 339, 1892.

By adding to these numbers for acids the heat of formation of water from its ions, Arrhenius has calculated the total heats of neutralisation of soda, and compared the results with the observed values for many acids.

	Calculated.	Observed.
Hydrochloric Acid -	13447	13740
Nitric            " -	13550	13680
Acetic            " -	13263	13400
Phosphoric       " -	14959	14830
Hydrofluoric     " -	16320	16270

The conductivity of a solution depends on two factors: (1) the dissociation, and (2) the frictional resistance offered by the solution to the passage of an ion through it. If we call the reciprocal of this resistance the ionic fluidity of the solution, the molecular conductivity will be proportional to the dissociation and to the ionic fluidity. At infinite dilution the dissociation is complete, and the ions are so far apart that no change in temperature can affect the state of dissociation. Any alteration in conductivity with change of temperature must then be due to an alteration in fluidity, and, therefore, the temperature coefficient of fluidity can be determined by measuring the temperature coefficient of conductivity at a dilution so great that the molecular conductivity has reached its limiting value. From the thermodynamical investigation it follows that, if the heat of formation is negative, that is, the heat of dissociation positive, the temperature coefficient of dissociation must be negative, so that the dissociation will decrease as the temperature rises. The increase in conductivity, shown by electrolytic solutions when they are heated, is, then, in general, due to the increase in ionic fluidity being greater than the decrease in dissociation. Now the table given above shows that the heats of dissociation are greater at 35° than they are at 21.5°, so that the negative temperature coefficient of dissociation must grow numerically greater as the temperature rises. If, at the same time, the positive temperature coefficient of ionic fluidity keeps constant, gets less, or in-



creases more slowly than the negative temperature coefficient of dissociation, it is evident that, at a certain temperature, the two will become equal, and that, beyond that temperature, any further heating will decrease the dissociation more than it increases the fluidity, so that the conductivity will again become less. The temperatures of maximum conductivity were calculated by Arrhenius for solutions of hypophosphoric and phosphoric acids, and shown to be  $57^{\circ}$  and  $78^{\circ}$  respectively. An experimental investigation actually gave maxima at  $55^{\circ}$  and  $75^{\circ}$ . More recently Sack<sup>1</sup> has found a maximum for copper sulphate solution at  $96^{\circ}$ . Calculation by Arrhenius' method gives  $99^{\circ}$  for a similar solution. Thus it appears that the thermal phenomena of electrolytic solutions are all satisfactorily explained by the dissociation theory.

An equally striking success has attended the application of the theory to the phenomena of the diffusion of dissolved electrolytes. A satisfactory account of the diffusion of non-conductors has been given by Nernst<sup>2</sup> and Planck.<sup>3</sup>

In any solution, the dissolved molecules are continually moving about in all directions. Therefore, in a given time, more molecules cross any fixed plane from the side on which the concentration is greater to that on which it is less than in the opposite direction. The more dilute parts of the liquid will thus grow stronger at the expense of those which were originally more concentrated, and this process will go on till the concentration is uniform throughout.

Now, the osmotic pressure of a solution depends on the concentration, and is approximately proportional to it, so that we may, for convenience, consider the variation in osmotic pressure, which exists in a solution of non-uniform concentration, to be the cause of the diffusion which goes on. Thus, if we put a layer of water over a solution of sugar, the osmotic pressure of the solution can be considered as driving the molecules of sugar into the water,

<sup>1</sup> *Wied. Ann.*, xliii., p. 212, 1891.

<sup>2</sup> *Zeits. für physikal. Chemie*, ii., p. 613, 1888; or, Nernst's *Theoretische Chemie*.

<sup>3</sup> *Wied. Ann.*, xl., p. 561, 1890.

and the driving force in any layer can be calculated from a knowledge of the variation in osmotic pressure gradient. If we replace the solution of sugar by one of hydrochloric acid, a further complication ensues. We know from Kohlrausch's work, that the velocity with which the hydrogen ions travel through a solution is, under an equal driving force, greater than the velocity of the chlorine ions, so that, at first, a separation goes on, positively charged hydrogen ions travelling quickly into the water, and negatively charged chlorine ions remaining behind. This at once explains the differences in potential observed when various solutions are put in contact with pure water. But, as this process of separation goes on, electrical forces, tending to prevent further separation, come into play between the oppositely charged ions, and presently a steady state is reached and the ions travel forward together. We can then equate the number of hydrogen ions crossing any layer in a given time under the influence of both the osmotic and the electric forces with the number of chlorine ions crossing the same layer, and from this calculate the actual rate of diffusion of the hydrochloric acid. The following table gives the observed and calculated values of the "diffusion constant," which may be defined as the number of gram-molecules of the dissolved substance which crosses unit area in one day when the osmotic pressure gradient is unity.

Substance.	D observed.	D calculated.
Hydrochloric acid - -	2'30	2'49
Nitric acid - - - -	2'22	2'27
Potash - - - - -	1'85	2'10
Soda - - - - -	1'40	1'45
Sodium chloride - -	1'11	1'12
„ nitrate - - - -	1'03	1'06
„ formate - - - -	0'95	0'95
„ acetate - - - -	0'78	0'79
Ammonium chloride -	1'33	1'44
Potassium nitrate -	1'30	1'38

In a similar way, the contact difference of potential between solutions of the same electrolyte at different con-

centrations or between solutions of two different electrolytes can be calculated. This is of great interest, for primary voltaic cells can be constructed, with a plate of the same metal for both electrodes, by placing the electrodes in solutions of different substances, or even in solutions of the same substance at different concentrations.

In the following table,<sup>1</sup>  $C_1$  and  $C_2$  denote the concentrations of the solutions round the opposite electrodes, and a comparison is made between the observed and the calculated values of the electromotive force.

Electrolyte.				$C_1$	$C_2$	E in volts (observed).	E in volts (calculated).
H Cl	-	-	-	0.105	0.018	0.0710	0.0717
"	-	-	-	.1	.01	.0926	.0939
H Br	-	-	-	.126	.0132	.0932	.0917
K Cl	-	-	-	.125	.0125	.0532	.0542
Na Cl	-	-	-	.125	.0125	.0402	.0408
Li Cl	-	-	-	.1	.01	.0354	.0336
NH <sub>4</sub> Cl	-	-	-	.1	.01	.0546	.0531
Na Br	-	-	-	.125	.0125	.0417	.0404
Na O <sub>2</sub> C <sub>2</sub> H <sub>3</sub>	-	-	-	.125	.0125	.066	.0604
Na OH	-	-	-	.235	.030	.0178	.0183
NH <sub>4</sub> OH	-	-	-	.305	.032	.024	.0188
K O H	-	-	-	.1	.01	.0348	.0298

The difference of potential between metals and electrolytes is explained in a similar manner. Nernst supposes that each metal in contact with an electrolyte has a definite solution pressure, analogous to the vapour pressure of a liquid, in consequence of which ions are detached from it, and go into solution, carrying their charges with them, and leaving the metal oppositely electrified. The electromotive force of an ordinary voltaic cell will depend on the difference between the solution pressures of the two electrodes, and could be calculated from Nernst's theory if these pressures were known. When a current passes, the ions of the metal with the smaller solution pressure are forced out of solution by the others, and deposited on the electrode.

The electromotive force of the cell

<sup>1</sup> W. Nernst, *Zeits. für physikal. Chemie*, iv., p. 161, 1889.

Ag | 0.1 normal Ag NO<sub>3</sub> | 1.0 normal K Cl with Ag Cl | Ag, in which silver electrodes are placed one in silver nitrate solution, and the other in silver chloride and potassium chloride, was calculated by Nernst to be 0.52 volt, and observed by Ostwald to be 0.51 volt.

The remarkable agreement shown between the results of experiment and the consequences deduced from the dissociation theory in the cases of the thermal phenomena and the laws of diffusion must be regarded as very strong evidence in favour of the substantial truth of that theory. No such agreement could arise unless there were at least a deep-seated analogy between the actual facts and the hypothesis on which the results have been worked out. It seems necessary to accept the view that the ions of good electrolytes are, in some way, free from each other for a considerable fractional part of their existence. This does not, however, exclude the possibility of the existence of molecular aggregates in solutions. Evidence of the existence of such aggregates has been collected by Pickering<sup>1</sup> and others, who have shown that, in varying the concentration of a solution, the physical properties often change at that point, at which its constituents are present in proportions corresponding to some simple molecular compound. Pickering made, for instance, a careful determination of the densities of solutions of sulphuric acid of different strengths, and drew a curve to show his results. Changes of curvature appeared at points corresponding to definite molecular proportions, and some of the hydrates thus indicated were subsequently isolated by crystallisation (*e.g.*, H<sub>2</sub>SO<sub>4</sub> · 4H<sub>2</sub>O, HCl · 3H<sub>2</sub>O). These changes can more readily be seen if a new curve is drawn between the concentration and the rate of change of density with the concentration (*i.e.*, the tangents at different points of the first curve). By this process of "differentiation," a series of straight lines is obtained, with breaks at the positions where, in the first curve, changes of curvature appeared. Similar figures were drawn for the electric conductivity, expansion by heat, contraction on formation, heat

<sup>1</sup> Watts' *Dictionary of Chemistry*, Art. Solutions II.

of dissolution, heat capacity, refractive index, magnetic rotation, and freezing point, and changes of curvature were found at the same points for all. Even when the solutions become very dilute, similar changes of curvature occur, and, although it is impossible to say, in such cases, whether or not the points correspond to definite molecular proportions, it seems fair to conclude that the changes are due to the same cause as those which appear in stronger solutions. As we go on adding water to a solution of sulphuric acid, heat continues to be evolved, so that it seems necessary to suppose that one acid molecule is able to combine with, or, at all events, to influence in some way, an enormous number of water molecules, and this idea is confirmed by other facts. For instance, the volume of a substance in solution is in general smaller than its volume in the solid state, and, in some cases, even appears to be negative, thus showing that the water has been compressed. Again, the molecular heat (*i.e.*, the product of the specific heat and the molecular weight) of a solution is sometimes actually less than that of the water present, so that the thermal capacity of the whole, or, at all events, a large part, of the water must have been affected.

There seems, then, considerable evidence to show that hydrates exist in solution, or, at all events, that there is a tendency towards the formation of such definite molecular aggregates. It was soon noticed that it was in the case of electrolytes that there was the clearest evidence of chemical action between the solvent and the body dissolved. This suggested the idea that chemical action was the condition necessary for ionisation, and the formation of complex molecules from which individual ions could be easily removed by collision with other aggregates, the meaning of conductivity.

By approaching the subject from two different sides we have, then, arrived at two conclusions. Firstly, that pairs of opposite ions must be separated, and the ions exist free from each other's influence, and, secondly, that there must be a tendency towards the formation of more or less stable molecular aggregates between salt and solvent.

It seems, however, that these two conclusions need not be mutually inconsistent. Since it is evident that one salt molecule can influence a large number of water molecules, it follows that the chemical forces are very far-reaching. Each particle of salt extends its influence over a considerable region round it, and the properties of the solution will depend on its percentage composition. It is natural, then, that, when the composition of the liquid passes through the value which corresponds to a definite molecular compound, the fact should appear in some modification of the physical properties, although no definite aggregate moving about as an independent physical molecule need be formed. There is, therefore, no objection to the view that the ions exist free enough from each other to enable them to play the part assigned them by the dissociation theory.

It is, nevertheless, remarkable that bodies, so stable when solid, should be dissociated in solution, but a study of the properties of the solvent throws some light on the difficulty. If the forces between the parts of the salt molecule are electrical in their nature, as is quite probable, it follows that, as J. J. Thomson has pointed out,<sup>1</sup> immersion in a medium like water, of high dielectric constant, will cause these forces to become much weaker. The effect is best explained by imagining a large mass of conducting material to be placed near two small spheres charged with opposite kinds of electricity. Each charged sphere attracts electricity of the opposite kind to the neighbouring parts of the conducting mass, and to this induced charge most of the sphere's lines of force will then converge. Its influence on other outside objects will be, therefore, much lessened, and consequently the force of attraction between the two little spheres will be much reduced. The effect of an insulator of high dielectric constant is similar in kind though rather less in magnitude. This may explain the differences observed in the molecular conductivities of the same salt dissolved in different solvents, such as water and alcohol, for example, for, other conditions being the same, the effect

<sup>1</sup> *Phil. Mag.*, xxxvi., p. 320, 1893.

of solvents in loosening the connection between two ions, *i.e.*, their relative ionisation powers, will be proportional to their dielectric constants.

As well as loosening the connection between the two spheres, the conducting body will attract each sphere to itself. There will be, therefore, chemical forces between the free ions and the mass of the solvent. These forces will, however, be, in general, equal in all directions, so that mobility is secured, the ions being passed on, under the influence of the external electromotive force, from one portion of solvent to another.

Readers who wish to examine the subject more in detail may be referred to a book on *Solution and Electrolysis* by the present writer, and, for further developments of the dissociation theory, to Ostwald's *Lehrbuch der Allgemeinen Chemie*, and to Nernst's *Theoretische Chemie*. Useful summaries will also be found in Watts' *Dictionary of Chemistry*.

CECIL DAMPIER WHETHAM.



## THE STUDY OF THE ANCIENT SEDIMENTS.

IN an article in the September number of "SCIENCE PROGRESS," attention was called to papers which appeared during the second half of the year 1894, which dealt with the Archæan and Lower Palæozoic Rocks; in the present paper it is proposed to consider writings treating of the Upper Palæozoic beds which were published during the same period. As usual the greater number of these are concerned with the coal-bearing deposits of various parts of the world.

In the September article certain papers were noticed which contained accounts of Upper as well as of Lower Palæozoic sediments, and it will be unnecessary to refer to these again, but before alluding to articles which are occupied with a description of beds belonging to a single geological system, I may allude to one paper containing notices of the various systems of the Upper Palæozoic rocks as developed in Central Asia (1). In the Southern Thian Shan, Middle Devonian rocks are found with the typical Mid-Devonian fossil *Stringocephalus Burtini*, and in the Central Kuen Lun is a Devonian *Stromatopora*-limestone. The Lower Carboniferous beds are also represented in those two regions, furnishing as they have done *Chonetes comoides* in the former, and *Streptorhynchus crenistria* in the latter region. The Upper Carboniferous (Moscow Stage) is found in W. Kuen Lun, as a *Fusulina*-limestone with *Spirifer mosquensis* and *Productus semireticulatus*. The uppermost Carboniferous strata are developed in S. Thian Shan, where they have yielded *Spirifer poststratus* and *Productus indicus*. In W. Kuen Lun are Permo-Carboniferous rocks with *Martinia planoconvexa*; whilst north of the Karakoram Pass are deposits which, formerly included in the Triassic, are now relegated to the Permian system.

It will be seen that our knowledge of the oceanic sediments formed contemporaneously with the abnormal Upper Carboniferous, Permo-Carboniferous and Permian deposits of Western Europe is rapidly increasing, and the time will soon come when the gaps in our information concerning the

interesting faunas connecting the Palæozoic and Mesozoic periods will be largely filled up; the supposed anomalies in the distribution of fossils which are still believed by many writers will then be satisfactorily explained.

There is little to add concerning the Devonian rocks; the only stratigraphical paper to notice is one treating of the rocks of the Altai Mountains (2). In this, Tschernyschew describes the fauna of the Krjukowsk-grube limestones, enumerating twenty species of fossils found therein, of which seven are new. The fauna of these limestones is comparable with that of the Coblenz group (Lower Devonian) of the Rhenish Provinces. The palæontology of the Devonian strata is enriched by another instalment of Traquair's *Monograph of the Fishes of the Old Red Sandstone of Britain* (3), in which the study of the *Asterolepidæ* is commenced, the genus *Asterolepis* itself being the subject of the contribution here noticed. The same author elsewhere (4) describes a new *Cephalaspis* from the Caithness Flagstones under the name of *C. magnifica*.

Turning to the Carboniferous strata, we may notice in the first place a paper of considerable importance to the stratigraphical geologist, giving as it does the mature judgment of a palæobotanist on the value of fossil plants as indices of horizons in the Carboniferous rocks; I refer to the Vice-president's address to the Royal Physical Society of Edinburgh (5). In this address Kidston states his belief that plants are more useful than mollusca for separating the Carboniferous strata: for this purpose the writer uses assemblages of plants and not single species. He remarks that "many of the Calciferous sandstone species do not pass into the Carboniferous Limestone series, though they have some species in common; still the floras of the two periods are very different as a whole. Again, we find very few of the Lower Coal-Measure plants passing up into the Upper Coal-Measures, and even the few that do pass up are among the rarest of Upper Coal-Measure species, whereas they are the commonest species in the Lower Coal-Measures; even from the Middle Coal-Measures very few pass into the Upper

Coal-Measures. The Middle and Lower Coal-Measures have a much greater similarity in their flora, but here, too, we find each series characterised by its fossil plants." Appended to this valuable address is a table showing the vertical distribution of the Coal plants in Britain.

Referring to the author's view that the plants are more useful than the mollusca for separating the Carboniferous strata, it may be remarked that at the present time such is undoubtedly the case, at any rate so far as Britain is concerned, owing largely to the care which has been exercised in studying these plants by a number of palæobotanists, amongst whom the author of the address is prominent; but one cannot help thinking that the time is soon coming when the animal remains of the Carboniferous strata will be recognised by British geologists as being of far more importance in classifying those strata than they at present suppose. Reference has been made in an earlier article to Waagen's views on the value of fossil animals as an aid to the classification of the Carboniferous deposits, and the Continental geologists are far ahead of us in the use they have made of the invertebrata for this purpose, but British geologists are waking up to the feeling that there is much work to be done amongst the Carboniferous rocks of our islands, and it is to be hoped that the British Association will give its official recognition (if it has not already done so) to the desirability of doing further work amongst these strata, by appointing a committee to study the distribution of their invertebrate remains. It may be confidently predicted that, when this is done, very considerable changes will be introduced amongst the time-honoured lists of Carboniferous fossils found in our text-books.

Passing on to consider additions recently made to our knowledge of the British Carboniferous rocks, we may briefly allude to two papers written by Professor Boyd Dawkins. As these treat of the interesting subject of the extension of the Coal-Measures beneath the newer rocks of Britain, a subject to which much attention was paid at the recent meeting of the British Association at Ipswich, it will be desirable ere long to devote a separate article to this important question, and meanwhile we may

very briefly notice Professor Boyd Dawkins' papers written during the period under review. The first of these treats of the Isle of Man (6). A thickness of 1368 feet of deposit is developed near Peel; these deposits are referred to the Permian system, and compared with the sandstones and "brockrams" of Cumberland, which are known to be of Permian age. At Llen Moar, south-west of the Point of Ayre, after passing through 167 feet of drift, a limestone (referred to the Carboniferous Limestone) was pierced. To the north of this saliferous marls, placed by the writer in the Trias, occur. He concludes "that the Coal-Measures of Whitehaven do not range so far south as the Isle of Man. If they do occur, the only spot where they can be hoped for is in the extreme north of the island, to the north of the Carboniferous Limestone."

The second paper by this author to which we have to refer deals with the occurrence of Coal-Measures in the south-east of England (7). He accepts the views of the late R. A. C. Godwin-Austen, lately elaborated by Bertrand after a study of the folds of France and the adjoining regions, that the great tectonic folds affecting the older strata are traceable by the folds affecting the newer rocks on the surface, though the minor folds are not to be detected in this way. Applying these views to the south-east of England, he points out that the folds occurring amongst the older rocks of the south-west of England are traceable into similar folds affecting the rocks of the south-east of the island. Commencing with the southern folds and working northwards, we have the following alternation of anticlinal and synclinal curves.

(1) The syncline marked by the Culm-Measures of Devonshire, which is traceable in an eastward direction by the superposed Tertiary basin of Hampshire. The coal beneath this he considers to be probably of the Culm type and therefore valueless.

(2) The North-Devon anticline, traceable eastward into the anticline of the Mesozoic rocks of the Vale of Wardour and of the Wealden area.

(3) The Mid-Somerset syncline, probably represented in the Wealden area by the highly faulted strata north of the Rother.

(4) The Pembroke-Mendip anticline, continued eastward into the anticline of the Vale of Pewsey near Devizes, and past various inliers at Ham, Kingsclere, Peasmarsh near Guildford, Westerham Common, Charing near Maidstone, and so through the faulted area south of Ashford to the sea, south of Hythe. (Professor Prestwich takes this farther north to the sea, north of Dover.)

(5) The South Welsh syncline, corresponding with the London Basin amongst the newer rocks. According to Professor Dawkins this syncline probably widens eastwards. He considers that the Coal-Measures which were reached by piercing the newer rocks at Burford in Oxfordshire occur there owing to the existence of this syncline (Professor Prestwich expects coal to be found in isolated basins in this syncline in the Isle of Thanet, Essex, Hertfordshire and Oxfordshire). Our author places the Dover Coal-Field in the southern part of this syncline and recommends search to the west of Dover. He also advocates trial shafts to be sunk in various parts of the eastern extension of the South Welsh syncline, which he believes to be broken up into isolated basins (such as are found to the west where there is no covering of Mesozoic rocks, as, for instance, the Bristol and Somersetshire Coal-Field, and that of the Forest of Dean). The detection of these basins will be the result of experimental borings. The paper is illustrated by a map showing the presumed eastward extension of the various western folds enumerated above.

We have no paper definitely devoted to the study of the Carboniferous beds of the European Continent to notice. Of Asiatic Carboniferous (or newer) deposits we have several accounts in the volume of the *Records of the Geological Survey of India* published in the latter half of 1894. W. Saise (8) takes the Karharbari Lower Coal-Seam as the base of the Barakar beds (a grouping previously made by T. H. Hughes), and evidence is given against the inclusion of some of the Coal-Seams in the underlying Talchir beds as proposed by Feistmantel. There is no evidence of unconformity between the Talchir and Barakar beds, but the different facies of the two groups justify their

separation. In this coal field "the total thickness of the whole of the Talchirs when best developed . . . cannot be more than 300 feet. The greatest thickness of Boulder bed is 22 feet, and yet we meet these beds all over the field."

It will be remembered that Waagen places the Talchir stage as the lowest of his three Permo-Carboniferous stages succeeding the highest or Ardwick stage of the Carboniferous proper; the Karharbari is the Middle, and the Artinsk the Upper stage of this Permo-Carboniferous group.

Griesbach (9) records a small patch of Carboniferous rocks probably brought up by faults amidst the Mesozoic beds of the Chitichun area, north-east of the Uttadhun Pass. They have yielded many fossils including *Fenestella*, *Lithodendron*, brachiopods of the families *Terebratulidæ*, *Spiriferidæ*, and *Productidæ*, some cephalopods and trilobites.

P. N. Bose (10) describes the Moulmein group of the Tenasserim Valley. Here a limestone has furnished *Lonsdaleia*, *Lithostrotion*, *Productus*, etc., of Carboniferous age, and on the supposition that this limestone belongs to the Moulmein group, of which the writer has scarcely any doubt, that group is Carboniferous. It contains worthless coals (the younger workable coals of the area being probably tertiary).

T. D. La Touche (11) describes the Bhangawanwalla Coal-Field of the Salt Range, and gives a map and section of the Coal-Field and adjoining district. Above the Salt-crystal pseudomorph group (of Cambrian age) is a Boulder bed succeeded by Coal-bearing beds. Above these are tertiary (nummulitic) beds.

There is one paper on the Carboniferous beds of Africa (12). Some time ago J. Walther announced the discovery of a Carboniferous Limestone in the Egypt-Arabian desert, which was referred by him to the Lower Carboniferous. In the light of further work the author refers these beds to the Upper Carboniferous, and we are thus furnished with a new area for the marine Upper Carboniferous strata. Amongst the fossils are *Fusulinella*, *Enteles ægyptiacus*, and other species, *Spirifer mosquensis*, *S. convolutus* var., and *Dielasma hastatum*. The beds seem most nearly related to the Carnic *Fusulina* limestone and the corresponding Gshelian division of Russia (stage of *Chonetes uralica*).



In Australia we have a record of the discovery of Coal near Sydney (13). After passing through 2917 feet of the beds appertaining to the Hawkesbury series (Triassic), the bore came to:—

Permo-Carboniferous,	{	Coal seam, 10 ft. 3 in.	}	1 ft. 9 in.
Newcastle series,		Clay, shale, and sandstone with <i>Vertebraria</i> .		

This genus *Vertebraria* is well known in the Permo-Carboniferous Damuda beds of India, with *Glossopteris*.

Professor David (14) discusses the position of the Australasian strata containing the *Glossopteris* flora about which so much discussion has arisen. He notes that it is the predominant plant, and is enormously abundant in the Permo-Carboniferous Coal-Measures of Queensland, New South Wales, and Tasmania. One doubtful locality (Arowa, N.S.W.) has been cited by M'Coy, where its age may be Carboniferous, but no well-established case has come under the author's notice where it has been found in Australia with *Lepidodendron* or *Rhacopteris*. In three doubtful cases of the occurrence of *Glossopteris* in association with Lower Mesozoic plants, the supposed *Glossopteris* may be *Sagenopteris*. In Queensland there is undoubted *Glossopteris* at a horizon which Jack considers Upper Cretaceous, but Norman-Taylor believes it to be Permo-Carboniferous, and the area where it occurs has not yet been mapped in detail.

Turning to the New World we meet with a paper by Professor Stevenson discussing a theoretical point. It is known that the volatile combustible matter in the Pennsylvania Coal decreases towards the east. The author's objections to hypotheses previously put forward to account for the change are given. He maintains that as regards its origin, the Anthracite of Pennsylvania does not differ from the bituminous coal of the Appalachian basin, "but because the great coal marsh from which sprang the many beds originated in the north-eastern corner of the basin, and extended thence on the advancing deltas formed by streams descending from the Appalachian highlands, the time during which the successive portions of the marsh would be exposed would be less and less as the distance from the north-east and northern border of the basin



increased, so that the extent of chemical change would decrease as the distance increased”.

Several papers on Carboniferous Palæontology remain to be noticed. Treating of fossil plants, we find a paper by Kidston (16) in which a new genus *Plumatopteris* is described. It is a fern which finds its nearest allies in certain species of *Archæopteris*. Six new species of plant are also described in the paper. Count Solms-Laubach (17) also contributes to our knowledge of palæobotany. Turning to Palæozoology, we may refer to the publication of Brongniart's work on fossil insects of the Palæozoic rocks, though this was published in 1893 (18), but as this beautiful work has been noticed elsewhere, it will be sufficient to quote the title. Dr. H. Woodward (19) describes two new *Phillipsiæ* from the “shales with limestones” referred by Tiddeman to the upper part of the Mountain Limestone series from the banks of the river Hodder, occurring in the disturbed tract of Carboniferous strata lying south of the Craven Fault. Thanks to this author's work on the trilobites of the British Carboniferous strata, this group of organisms will probably be of considerable value in the immediate future in classifying the Carboniferous strata, as it has already been found in separating the various members of the Lower Palæozoic Strata.

The last work to notice is the commencement of a Monograph on *Carbonicola*, *Anthracomya*, and *Naiadites* by Dr. Wheelton Hind (20). Professor Hull has spoken of this group of shells as having been “a bane to palæontologists,” and there has certainly been great confusion both with regard to the synonymy of the group, and the habitat of the forms belonging to it.

This confusion, thanks to the author of the Monograph under consideration, seems likely to be removed. He has “been reluctantly obliged to acknowledge that in two, at least, of the three genera to be described in this Monograph the names now in use must be abandoned for others which have the priority. M'Coy's name of *Carbonicola*, though accompanied by a partly erroneous diagnosis, is undoubtedly a few months older than King's *Anthracosia*, in which, too, the hinge characters described belong to a species and not

to the genus. And, also, there is no doubt that Professor J. W. Dawson's *Naiadites* is older than Salter's *Anthracoptera*, although Dawson's genus originally contained members of all the genera to be described in this work." Further information concerning the synonymy of the group may be obtained by reference to a paper by the present author published in the *Quarterly Journal of the Geological Society*, which contains a list drawn up by E. T. Newton, also in a paper by Professor Amalitsky in the *Quarterly Journal* for 1895, and in the report of the discussion thereon. With regard to the conditions under which the group lived, it is well known that Salter, in opposition to nearly all other authorities, upheld its marine character. The author presents and weighs all the available evidence bearing upon this question, and decides essentially in favour of a freshwater habitat. He sums up as follows: "On the whole very little positive evidence can be brought forward on behalf of a marine habitat for these shells, while there is, to say the least, a fair amount of presumption that they lived under freshwater conditions. It may be, however, that we have in the occurrence of *Carbonicola* and *Naiadites* with various marine forms at the base only of the Coal-Measures an example of a genus changing its habitat. It is probable that all molluscan forms were originally marine in habit, and that by modification and adaptation some few forms became able to exist in fresh water; and it is also probable that this adaptation took place at different times, and is even going on now, to wit, the discovery of *Hydrobia Jenkinsi* in inland canals of late years, which shell had till that time been only known under estuarine conditions." The author's view is thus substantially in accord with that previously expressed by Prestwich, John Young, Green, and others. The present contribution to this Monograph contains a description of the British species of the genus *Carbonicola* (*Anthracosia*).

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## CARL LUDWIG.

THE development of the science of life has more than that of other knowledge gone forward in our days under the guidance and direction of just a *few* transcendent teachers. The scope and methods of modern physiology, in so far as it claims to be an exact and truth-loving science, lie confined within the limits which Johannes Müller and Carl Ludwig have set. We must go back to the Athenian days of Stoa and of Academy to find a personal influence as great as that exercised by the last great teacher. Life is for us the tritest, but at the same time the most marvellous, and the most awe-inspiring reality. Strange therefore that even in these days its fundamental doctrines should obtain but few masters for its exposition. In this respect we may perhaps detect a secret link between it and metaphysics, from whose speculative views physiology—a science of facts and substance—stands totally remote.

In Germany no single branch of natural science can boast a greater teacher than Carl Ludwig. Many are disposed to rank the scholar, the investigator above the teacher. A false conception! Who can seriously so underrate the latter, for he also "must by hard fighting have won conviction for himself in regions where no other could come to his aid, and must, in other words, have laboured on the confines of human knowledge, and conquered new dominion for it"?<sup>1</sup> A great teacher in the true sense is even superior to a great investigator; to the latter the meed of acknowledgment is accorded, if he has widened the limits at any special point of the vast territory; from the former however is demanded, that he be master of the whole, have an eye for every detail, and in wise foresight prepare for its fulfilment what the future has to ripen. The possession of these latter qualities by Ludwig is most conspicuous in his *Lehrbuch der Physiologie*, and through-

<sup>1</sup> Helmholtz, *Über die akad. Freiheit u. s. n. Vorträge und Reden*, ii., p. 208.

out his activity as an academic teacher. What science owes to his own hands, and to his mind working through his numerous pupils, can be gathered from the annals of the laboratories of Marburg, Zürich, Vienna and Leipsic. Those who have not enjoyed his personal teaching are enabled by these to judge of the immense mass of new facts, the significant and ingenious method, and the extent of his investigations. These papers discover what a mighty plan lay at the root of Ludwig's labours, and with what firm perseverance he unwearily tried from all sides to decipher the problems of life. A number of men, well known to the science, with noble subordination ranked themselves as combatants in his general host, beside many simple comrades, who steadfastly followed the gifted leader; these shared his struggles and most toilsome victories. But it is from Ludwig's *Lehrbuch* and from his lectures that one can gain the deepest insight into the activities of his penetrating mind. In these the master ever held in prospect the whole territory, and the attentive follower came to understand *how* physiology is to be studied.

A thinker of genius, a philosopher (Arthur Schopenhauer) has declared that not the *Why*, but the *How* of things is the real task of knowledge. A modest, also a profound, judgment from the representative of a science in which the mind can unrestrainedly expand its wings, and in phantasy may order and measure things and ideas as its imagination may desire. Ludwig's greatest merit lies in the fact that he would not have the science of life treated otherwise than from the point of view of a study modestly confined to the nexus of natural laws governing the workings of the animal body.

The oft-quoted sentence introductory to his text-book: "Scientific physiology has for its task the establishment of the functions of the animal body, and the tracing of them consequentially from the elementary conditions of it,"<sup>1</sup> expresses this with absolute clearness. His whole life work

<sup>1</sup> Die wissenschaftliche Physiologie hat die Aufgabe die Leistungen des Thierleibes festzustellen und sie aus den elementaren Bedingungen derselben mit Notwendigkeit herzuleiten.

has its source and spring in this principle. It will therefore hardly be deemed mere chance that he surpassed as a deviser of ingenious methods. What Kirchhoff did for mechanics Ludwig did for physiology. Unlike as the two men were in the outward form of expression, an unlikeness made still greater by the difference of the problems to which the two men devoted themselves, yet that difference between them was largely superficial, for they were so essentially alike in their conception as to how an exact science shall be treated. The sensation caused by Kirchhoff's introduction to mechanics is well-known history ; and how foreign and secretly unsympathetic the task appeared to many minds—to describe, perfectly and in the simplest manner, the movements occurring in nature. To have introduced this same conception into physiology long before Kirchhoff published his celebrated work—or successfully worked it out—is Ludwig's significant achievement. The daring of it was the daring of genius, and formed a link of close though deep relationship between the two contemporary investigators. Physiology owes to Ludwig no small number of discoveries of the highest importance; yet as a discoverer Ludwig's position is not unique ; our century has been a most splendid era for discoveries in physiology. It is the method of investigation, the manner in which the complicated phenomena of animal life were treated by Ludwig and his school that struck so brilliant light in the dim field previously covered by a cloud of speculations.

Ludwig like many other great savants had as a writer much of the artist in him. The addresses and the more popular lectures which he delivered occasionally are real masterpieces of composition and poetic imagery. This same gift of poetic imagination, this same remarkable talent for stating facts in a figurative and symbolic manner, guided his pen, when he—as he very often did himself—wrote the papers embodying the results of the researches of his pupils. The real attitude of Ludwig's mind as an investigator, the sober and matter-of-fact spirit in which he grasped the problems of animal life, has therefore sometimes been obscured by his artistic nature. Ludwig treated physiology

in his lectures in a manner quite different to that usual with many lecturers on natural science. He contented himself with drawing a simple logically-constructed sketch of the known facts. He who in some of his publications and in private conversation betrayed a charmingly artistic imagination, and sometimes an almost mystic foresight, showed in his lectures almost bald conciseness, and a pitiless logic. A great number of ideas, to which some teachers attach deep meaning, he ruthlessly treated as mere definitions, indispensable as symbols for the shorthand description of facts. It was with him a matter of conscience to impress on his pupils that inductive philosophy building upon correct observation forms the only basis for understanding the functions of the organism. Being well aware of the seriousness of the task of educating young men, who one day would be called upon to alleviate the agony of human suffering, to face with a firm eye a state of things against which speculative reasoning is an impotent weapon, he gave them for equipment the most precious instruments which he himself possessed: his conceptions of the how of life together with the best methods for studying it objectively.

It is no unnecessary digression to dwell here on the personal characteristics of the great physiologist. It was his personality that made him so great a teacher, and it was as teacher that he exerted indubitably an unparalleled influence over contemporary physiology. Nearly 300 pupils have, under his guidance, contributed by research to the furtherance of biology. Especially intimate were the relations between the Leipsic laboratory and British and American physiologists. Germany, Austria, Italy, and Scandinavia form a strong contingent of Ludwig's pupils, many of whom rank as the foremost physiologists in their respective countries, and, as his true heirs, work on in the spirit of his school. The school of Russian physiology owes its being almost entirely to Ludwig. Although, as already stated, Ludwig's power of attraction as a teacher was largely due to his personality, deeper reasons further contributed. Ludwig devoted his attention to



nearly the whole range of physiology, and not solely to a few special branches, so that, however varied the inclinations or the talents of the pupils were, he was able to allot to each a suitable task. The single field that lies untouched by him is, perhaps, the physiology of the senses; von Kries in his memorial of his late master has explained the wherefore of this, namely, that Ludwig entertained mistrust of the subjective methods indispensable to this kind of investigation. As a natural consequence of the wide field of work occupied in Ludwig's Institute, all the collateral sciences were enlisted to aid, macro- and microscopic anatomy, physics, and chemistry. Ludwig understood in a masterly way how to utilise the skill and knowledge of specialists in those sciences for the purposes of physiology. Hence arose often an interesting relation between teacher and pupil; the pupil himself, sometimes a master in his own particular subject, willingly followed the inspiration of a man who led his talents to new fields of observation. From this happy collaboration a number of papers took origin in Ludwig's laboratory, intrinsically valuable from the accuracy and importance of their histological, chemical, or physical methods, and at the same time full of deep interest from their results in regard to purely biological problems. On the other hand, Ludwig knew how to attach to himself numerous men who wished later on to follow the more practical part of medicine, for the investigations of the Ludwig school were practical in the best sense of the word, being always directed to functions actually occurring in the animal body, and, for the greatest part, best observed through examination of the living animal. A brilliant feature of his teaching was his sketching plans of work for pupils, and in conducting the execution of them. In most cases his worker had to continue where another had left off; and it is a character and peculiar feature of the Ludwig Arbeiten, that not one among them all ends with a summing up of the results gained, but merely with modestly pointing to the new questions arising out of the work done. The very first conference with Ludwig usually showed the pupil

that before him lay a path leading toward something practical with good prospect of success. Ludwig sketched an extended plan and very often entrusted to his pupils the first use of an apparatus which he had himself invented and constructed in view of questions yet to be solved. How much of the actual work he and his able mechanician Salvenmoser did themselves depended on the capability of the pupil. But despite his plan already laid down according to certain lines, and despite his gift of lucid foresight of the nexus of things physiological, the result of the experiment alone was guide for all further steps in the investigation. "The best that we can say is what nature itself says to us;" these words, which his revered teacher said a few months ago to the writer of this paper, were the precept he always followed, a precept which seems a matter of course, and yet is so often subject to the temptation of being neglected.

Ludwig's scientific achievements in physiology must be viewed as to their importance, firstly, for the introduction of new methods; secondly, for their shedding new light on numerous of the most complex processes of the animal machinery. Foremost must be placed the invention of the graphic method. It is only fair to say that Thomas Young, stamping with his remarkable genius each manifold subject that he treated, had before Ludwig invented this method. But it was through Ludwig's quite independent reinvention that it became common property, not alone of physiologists, but also of all other scientific men, of physicists, astronomers, and others. When, in the year 1847, Ludwig studied the influence of the respiratory movements on the circulation in the aortic system, he, for the first time, placed in the open limb of the mercury manometer connected with the artery a float provided with a pen, and let this record the oscillations of the mercury on a drum revolving with a constant velocity. This first recording apparatus—the Ludwig Kymographion—is now a standard apparatus, always applied to if we want to question the throbbing heart, the beating pulse, the breathing breast, and, indirectly, by their answers, the nervous system regulating these wonderful vital actions. The value of this in-

vention cannot be overrated. We younger workers are so accustomed to the graphic method, and look upon it as such a matter of course, that we can hardly conceive the extent to which it has revolutionised biological science. The observing eye replaced the speculating mind in studying functions of animal life, hitherto inaccessible to any experimental research. The course of the most intricate processes and their dependence on various conditions, natural and artificial, could be expressed as measurements of tracings on a surface that could be kept as an objective document for an indefinite time. It is the want of the graphic method in previous generations that accounts for their prevailing ignorance and for their often absurd ideas about the most common actions of life, albeit in those generations there were plenty of mental achievements of the most brilliant kind.

Only three years after the invention of the graphic method, Helmholtz made by its use—besides the appliance of the Jouillet method of measurement of time—his great discovery regarding the velocity of nerve-energy, by which the foundation of a new branch of biological science, namely, that of experimental psychology, was laid.

In close connection with the kymographion, and supplementary to it, appeared in Ludwig's laboratory a great number of other new instruments for estimating time-relations; these were chronographs, clockworks for making and breaking electric currents at given intervals, the rheometer, used to measure the amount of blood flowing through a vessel in a unit of time, instruments for study of the pulse (sphygmographs), etc. For the examination of the gases in the blood and in the lymph, Ludwig constructed a gas-pump besides various other appliances, which served for a simplification of the measurement of them. The Leipzig physiological laboratory with its complete arrangements for graphic and measuring methods, wherever vital processes, in spite of their subtlety, permitted, has served as model for all institutions since erected. When this year the third International Physiological Congress met in the new and magnificent institution of Berne, Professor Hugo Kronecker, himself a pupil of Ludwig, and universally regarded as the heir of his genius.

for physiological method, could describe this, the youngest Physiological Institute in Europe, an offspring of his great master.

In the last century Albrecht von Haller had formed and, in a certain sense, proved his celebrated doctrine of irritability. It was reserved for Ludwig to shed full light on the deep importance of this principle, and make it available for scientific research by introducing his second great method into physiology. He perfused with blood the organs of the dead animal under the conditions appropriate to each, and awakened in this manner the seeming dead to new life. The excised muscle, heart, lung, kidney, testicle, liver, and the walls of the blood-vessels performed vital processes, the course of which was only subject to the variable conditions of the experimenter. And as evidence of these inner processes, the chemical examination of the perfused blood revealed the interchanges of gases and matter which had taken place between the tissue and the blood, the chemical composition of which had been previously regulated according to the purposes of the investigation. The success of this method not alone proved decisively that each tissue had its own irritability, but it also showed that the entity, which we call life, is composed of a whole set of lives in great extent independent of each other; hereby was opened a new view for the co-ordination of the organism. The analytic method, that most proper to all exact scientific research, was hereby not exactly introduced into biology, but gained its characteristic physiological form. The elementary functions of, for instance, nerve and muscle had been investigated by good methods, and in certain sections of physiology a clearness of description had been developed which could vie with that of physics. But in these investigations a complex of external purely physical and internal semi-vital phenomena had been made to interact so that it remains an open question as to where in the results the line between vital and not vital process should be set. With Ludwig's new method, it was quite different. Here the experimenter simply tried to offer to the isolated organ, as far as possible, the conditions that surround it in the body, and all the results were

phenomena due to the organ itself. Even when an organ was subjected, for the sake of investigation, to conditions not normally existing in the body, the tissues, if they reacted at all, could only react in virtue of their cellular life. This method therefore also benefits pathology in a great measure. Ludwig had an especial liking for this method.

Time was when anatomy and physiology were invariably housed together, and the latter stood to the former in the relation of a servant. No doubt anatomy is the basis of all sound physiological research, but the fetters which chained the younger to the elder science had to be loosed to make its free development possible. It was in the middle of this century that Ludwig together with Du Bois Reymond and Helmholtz sought to give physiology the character of a mechanical science, and thenceforth to physics and chemistry were assigned the leading parts. The adherents of the older morphological method in biology saw with dissatisfaction this new departure, and the feuds between Ludwig and Rudolf Wagner stand out as historic memorials of those days. This antagonism has remained in a certain degree to the present day; the adherents of morphology who have taken advantage of the theory of evolution and glorying in its recent extraordinary development not seldom reproach the Ludwig school with disregarding the morphological principles of animal organisation. But it was quite erroneous to believe that Ludwig ever relinquished the sure foundation of anatomy. The contrary rather is true, as might be expected of a man who began his career as a teacher of anatomy. The manner in which he differed from previous as from later anatomists has been his new conception of the task of anatomy in relation to physiology. Here he enriched the latter science with a third innovation of method. He started a physiological or, as I should like to call it, a mechanical anatomy. The structure of the tissues and of the organs of the animal body interested him in so far as by their exact description was rendered visible the solution of mechanical problems offered by it. Not the breaking up of a machine into any arbitrary number of infinitesimal particles, not a seeking after the probable origin of the

elementary components—a question of no small interest from quite another point of view—but the building up of single parts into a whole was his mode of describing a machine, thus leading to a knowledge of its powers.

Thus it has come to pass, that the arrangement of the blood-vessels in nearly all the parts of the body has been studied by Ludwig and his pupils, especially in the kidney, the eye, the muscle, the various glands, the small intestine, the ear, the skin and the larynx. His descriptions of the special patterns of circulation special to particular organs awaken distinct conceptions of a most wonderful machinery; he used in his lectures to deduce some of the most intricate functions of the organs from anatomical facts about the vascular apparatus and in a most forcible manner. His theory of the mechanism of the secretion of urine, for instance, is to a great degree based on the insight which his studies on the structure of the kidney afforded him. It was his genius for mechanical anatomy that led him to investigate the lymphatic system, where he showed that with its network of delicate and minute vessels honeycombing the tissues throughout the major portion of the body it forms an apparatus, worked and regulated by mechanical rules. He often used to urge that the anatomy of muscle should be treated as a chapter of dynamics, and the researches of Braune and Fischer have in a very promising manner been conducted according to his principle. His keen appreciation of anatomical facts guided him in devising methods previously unexampled in precision by which light was shed on the functions and structure of the spinal cord, and numerous special centres were discovered in the medulla oblongata. I have tried to show that it was characteristic of him to open out to auxiliary sciences and to their methods distinct physiological applications. No better instance can be quoted than the method, the working out of which he entrusted to his pupil the now celebrated neurologist Flechsig. By this method, his own discovery, Ludwig by means of a pupil obtained new facts of first-rate importance for the physiology of the brain and spinal cord.

Unlike the methods of embryology as handled by mor-

phologists—in Ludwig's developmental method of study of the central nervous system a purely physiological principle is laid hold of, and in a physiological spirit the further researches employing it have been carried on. Flechsig's *Hirn Anatomie* was in later years Ludwig's *Hirn Physiologie*. I well remember how in his lectures he inserted the latest discoveries in the anatomy of the central nervous system with the utmost promptitude. His bent of mind in this direction he reveals exquisitely in his *Lehrbuch*,<sup>1</sup> in a well-known passage which I will quote fully to give at the same time a sample of its amusing and yet powerful style: "Wem die zahllosen Schwierigkeiten vor Augen treten, welche sich hier der Untersuchung entgegen werfen und wer, im Geiste den wunderbaren Bau des Hirns schauend, von Staunen ergriffen ist über die Leistungen dieses zarten und verschlungenen Gefüges, der wird gewiss mit Abscheu sich wegwenden von den rohen Versuchen jener Klasse von Henkern, welche blindlings durch den Schädel hindurch mit Nadeln und Messern in das feinste aller Gebilde stechen und schneiden unter dem dreisten Vorgeben, der Wissenschaft einen Dienst zu leisten. Das Beginnen dieser Hirnbohrer ist kaum weniger sinnvoll als das Bestreben, durch Schüsse aus Flinten und Pistolen, die man in eine Cylinderuhr sendet, die Functionen ihrer Räder und Federn zu ermitteln." If we compare the modern delicate methods of experimental research on the brain with those of Magendie, Flourens and others, to whom the just quoted passage refers, we cannot but be grateful to the great man who here saw that anatomy is an essential basis of experiment.

Ludwig was the first to make chemical considerations an integral part of experimental research in physiology. With his accustomed genius for analytical method he contrived to vary the chemical conditions, and thereby induced most important vital reactions. While he left the study of the constituents of the animal body to chemists, he undertook an examination of the chemical processes in the various organs and made these work to his bid and call. Like

<sup>1</sup> Vol. ii., p. 203, 2nd edition. Leipzig, 1858.



physics and anatomy, chemistry also became in his hands a tool for the service of experimental biology.

A record which, in pages preceding mine, Professor Stirling furnishes of the work of the great physiologist, gives the reader an enumeration of the discoveries and researches of Carl Ludwig. In closing my sketch of the master I would pay one more last tribute to his great personality. For us who knew Ludwig in the grandeur of his patriarchal age, "hero-worship" was no idle phrase. He was for us a sage and a priest; he inspired us with warm-hearted admiration for the wonders and beauties which nature willingly reveals when asked with conscientiousness and assiduity; he taught us modesty by impressing upon us how little we knew and how small our powers compared with those of creative nature. But he did still more for us; he, the great investigator of animal life, never forgot its higher, ethical aspects; without any ostentation or pretentious moralising he tried to imbue us with the feeling that knowledge of life, as he understood it, leads to the recognition of a path of duty and of stern ideals. I have read or heard scarcely anything that could vie, for instance, with the simple but beautiful words he spoke to us all once suddenly, when lecturing on pain: "*Der Schmerz ist vielleicht das einzige Reale, was es auf der Welt giebt. Alle Cultur geht darauf aus, das zu beseitigen, was Schmerz verursacht, und die höhere Cultur ist bestrebt das zu beseitigen, was auch nur in der Vorstellung Schmerz erwecken konnte.*"

LEON ASHER.